PREPARATION OF PHENOLIC RESINS FROM PYROLYTIC OIL PHENOLIC EXTRACT

A THESIS

SUBMITTED TO THE FACULTY OF ATLANTA UNIVERSITY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF MASTER OF SCIENCE

BY

SAMUEL JOHNSON

DEPARTMENT OF CHEMISTRY

ATLANTA, GEORGIA

MAY 1979

ABSTRACT

CHEMISTRY

JOHNSON, SAMUEL L. B.A., DILLARD UNIVERSITY

PREPARATION OF PHENOLIC RESINS FROM PYROLYTIC OIL PHENOLIC EXTRACT

Advisor: Professor M. B. Polk

Thesis dated May 1979

Preparation of a phenolic resin of the resole type from the phenolic components of pyrolytic oil was successfully performed. Separation of these components was carried out using solvent extraction techniques, and a separation scheme which divided the components of the oil into different chemical classes.

Effective identification and characterization of the resinous material was made by molecular weight determination, infrared spectroscopy, elemental quantitative analysis, differential thermal analysis, and solvent solubility.

The product obtained was of high molecular weight and the proposed method of separation and polymerization was substantiated.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Preparation of Phenolic Resins from Pyrolytic Oil Phenolic Extract

Pyrolysis represents a means for converting once thought of waste materials from forestry, agriculture, and municipal systems to useful products. These products could prove useful as alternative fuel sources. Since many chemicals in sufficient quantities are present in the oils, reactions of many types could lead to other by-products. One such reaction is the formation of phenolic resins.

Phenolic resins are a host of products resulting from the reaction of phenols with aldehydes. These phenols could be phenol itself, resorcinol (meta-hydroxy phenol), or alkyl substituted derivatives such as cresols, xylenols, p-tert-butyl phenol and p-phenyl phenol.[1] The aldehyde used is almost always formaldehyde, but acetaldehyde and furfuraldehyde are sometimes used. Most phenolic resins produced are heat hardenable and will form three-dimensional thermosets under the influence of heat. Therefore, reaction uniformity in these condensations must be obtained by careful control of reaction conditions such as temperature of condensation, catalyst concentrations, and pH. At the early stages the reaction is quite exothermic, which presented many problems in early attempts to polymerize phenol and formaldehyde to an infusible, non-reactive state.

A. Smith was granted the first patent for a phenolic resin product when in 1899 he described a method for the cost cured resin substituted for hard rubbers.[2] But phenolics had their first reported beginning in

1872 by Baeyer, who found that phenol and aldehydes combined in the presence of an acid catalyst to give an unmanageable resinous mass.[3] There were numerous other attempts to identify procedures, processes and conditions for polymerization and determinations of mechanisms and market value. Michael reported the use of an alkaline catalyst to give a resinous material.[4] Kleeberg was given credit as the first to work with formaldehyde in 1891,[5] and Luft followed Kleeberg and Smith's work by using a higher molar ratio of phenol to aldehyde.[6] Smith also made attempts to commercialize his product-procedure. It wasn't until Baekland started working with phenols and formaldehyde in 1905 that the age of phenolic resins was born. By 1907 he had designed and commercialized processes for the production of a controllable, industrially important and valuable resin. He had established the difference between acid and base catalyzed reactions with varying molar ratios of phenol to formaldehyde. Most importantly, however, was his idea to use counter-pressure during the curing process to prevent bubbles and foaming from heat that had plagued previous attempts to make a solid, strong, cured resinous object.[7] He obtained his patents after waiting 2 years, in 1909, at which time he disclosed his research findings in a paper delivered before the American Chemical Society on February 5, 1909.[8] Baekland further showed that with an excess of formaldehyde to phenol, the end-product was still heat reactive with acid or base catalysis; but only the alkaline catalyst would give a controllable reaction scheme to product. Having control of the thermo-setting reactions he then defined the following stages of polymerization:

1) the initial stage resole, A, in which the polymer was

either liquid or dehydrated to a solid but soluble in simple organic solvents and fusible;

2) a second stage resitol, B, in which the resin was solid, insoluble but swelled by solvents and infusible but softened by heat; and

3) a third stage resite, C, in which it was infusible, insoluble, and not softened with heat or swollen with solvent.[9]

Woods of different types can be pyrolyzed to obtain among other things, condensed pyrolytic oils. It has been verified by Hawley and Wise that the products from wood pyrolysis are composed of low molecular weight aldehydes, ketones, alcohols, aliphatic acids, phenols and other aromatic compounds.[10] In a recent report by Panasyuk and co-workers, there was successful utilization of lignins of various plant materials to obtain phenols, such as m-cresol from sunflower husks and cottonseed hulls. Coniferous wood yielded considerable amounts of guaiacol and small amounts of cresols.[11] In another report Shmulevskaya and Liverovskii predicted the increased use of bark in wood gasification procedures.[12] They found that the use of a two-step gasification process of spruce bark, would give an increase in the amount of phenols obtained if the distillation of the sedimentation tars were continued. Also, the reactivity of the phenols obtained were comparable to those obtained from wood gasification. The reactivity of phenols from woods were decreased by the high percentage of methoxide (MEO) content. This decreases the functionality and, therefore, their ability to polymerize.

However, the phenols could be activated by demethylation and could be used for the manufacture of phenol-formaldehyde resins suitable as wood-particle board binders.[13]

Wood pyrolysis to obtain the oils used in this report involved the pyrolysis of pine bark and sawdust which was heated to a very high temperature in a special isothermal furnace. The conditions are controlled in such a way that the wood materials don't burn to ash. This is mainly done by using a limited amount of air throughout the process.[14] There are several products recovered; one is a non-condensible gas, a second charcoal and a third a heavy condensed oil labeled project B-469 condensor oil for this research project.

The separation of phenols from the pyrolytic oils was carried out by solvent extraction. Solvent extraction is used in organic chemistry for the separation and isolation of dissolved compounds from solutions. This process operates on the principle of the distribution law. If the ratio of the amount of a given component present in each phase differs significantly from that of another, a separation of the two is potentially possible.[15] Solubility of organic compounds is directly related to the molecular structure of the solute. Extraction with chemically active solvents (dilute alkali and acid solutions), depends on the formation of soluble salts which are insoluble in chemically inert solvents (ethers, alcohols, etc.). The solubility of compounds in these inert solvents can be ascertained with fair success using the empirical rule "like dissolves like."

Phenolic resins have a variety of uses throughout the industrial world. It is because of their diverse and varied properties that phenolics have found their way into many facets of production. In its more than

60 years in existence it has held its own in a world of vast technological advancement. This feat is more than adequately accounted for by its heat resistance at over 400°F in continuous service; excellent electrical and insulating properties; good dimensional stability with precise dimensional tolerance; comparatively little expansion, shrinkage, or changes in flexibility over a broad temperature range; excellent durability and stability under aging conditions; not supporting combustion and its self-extinguishing property.[16] Some of the specific uses of these resins are as molding materials, laminating resins, abrasives, friction materials, brake linings, thermal insulation, plywood binders, bonding organic fibers, and protective coatings. The resin may be delivered to the user ready to be cured (resole or resitol) or in the novalac state in which a hardener, commonly (hexamethylenetetramine), will be added. This potentially allows the users to handle the resin in this low-molecular weight, fusible, soluble state which can be reacted to a high molecular weight, strong, heat-resistant material. The two major factors determining the course of a typical polymerization are the ratio of phenol to formaldehyde and the type of catalyst used (acid or base). When the ratio of formaldehyde to phenol exceeds one, this sets the stage for the polymerization of a controllable resin. When an acid catalyst is used the reaction proceeds at an uncontrollable rate and becomes very exothermic. The use of an alkaline catalyst will also increase the rate of reaction, but at a manageable rate, with lower temperatures of polymerization. Thus, a very low molecular weight resin may be obtained which is water soluble at room temperature and useful for impregnation or saturation of some substrates.[17] If a higher molecular weight resin is desired, the resin can be further reacted by

dehydration to form a solid grindable resin which is still heat reactive. In both states the resin is still heat reactive and can be further reacted to an infusible crosslinked state in subsequent use.

The production of the resole polymer involves greater control over the product desired because the low temperature slows down the reaction of phenol and formaldehyde to polymer. Also, the resin in the a and b-stages can be reacted to the thermoset in one step by continuing the dehydration period for a number of hours. Unlike the resole polymer, the novalac resins (acid catalysis) represent a completed reaction and cannot continue to increase in molecular weight through condensation during the course of the polymerization. Novalacs contain no reactive groups that may produce crosslinking, and therefore, must be subsequently cured (crosslinked) by addition of a polyfunctional compound that will react with phenol. The compound most often used is hexamethylenetetramine (hexa).[18] The preparation of the uncured novalac may be best represented by the reaction in Fig. 1 and the subsequent crosslinked structure formed on curing with hexamethylenetetramine as in Fig. 2.

According to Odin, the initial reactions of phenol with formaldehyde leads to the formation of a mixture of mononuclear methylol phenols (I), dinuclear (II), and polynuclear (III) compounds (Figure 3).[19]

In view of the fact that a base catalyst is used and the formaldehyde is in excess, each of these compounds is termed a resole prepolymer, and their formation is part of the first phase of polymerization.[20] The second phase involves condensation, preceeding to crosslinking upon further heating. Crosslinking is the process by which one-step and

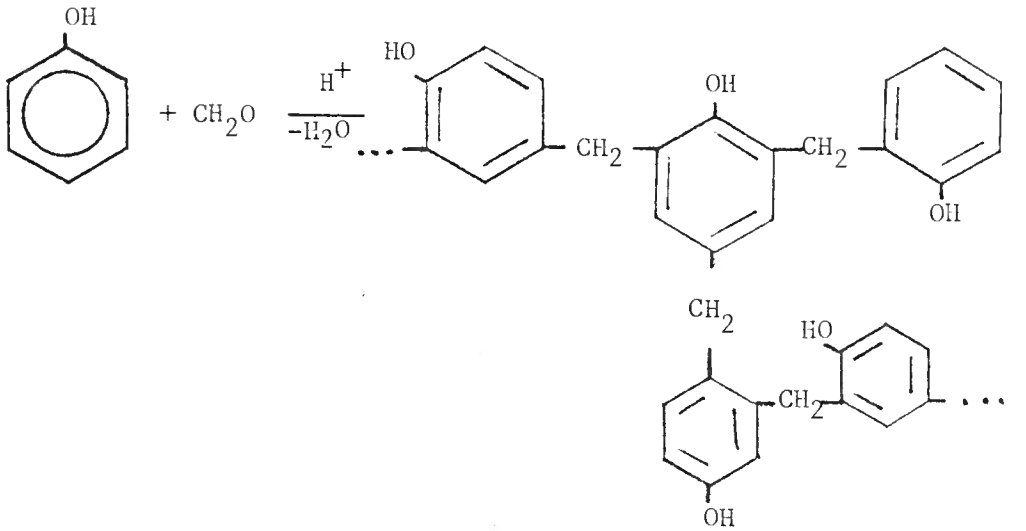


Fig. 1. Reaction of Phenol to Uncured Structure.

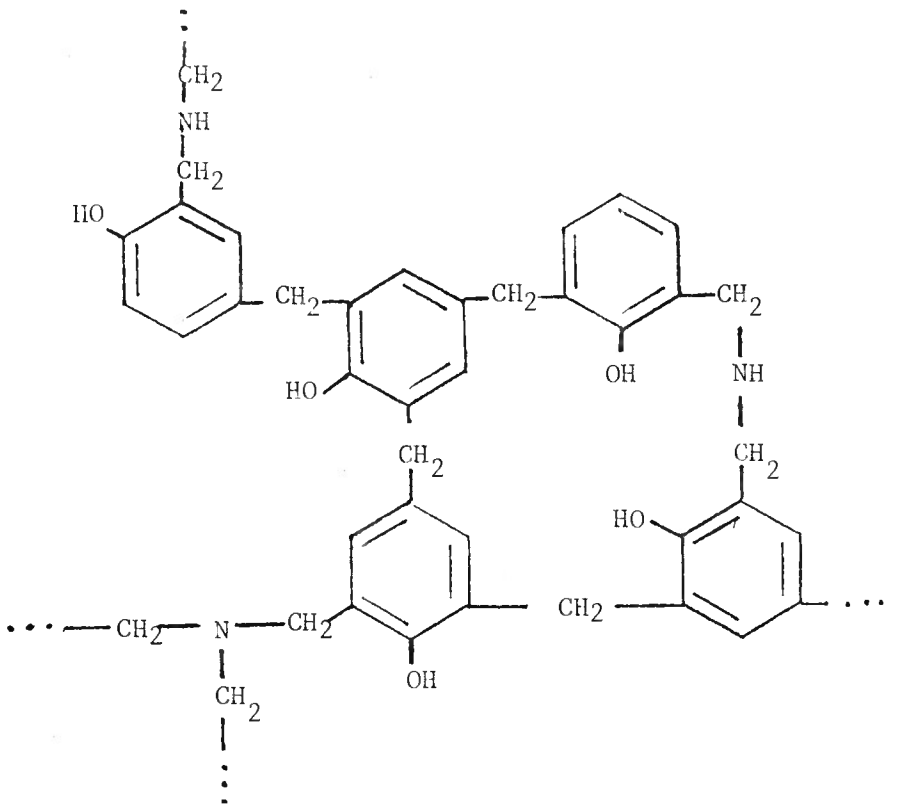


Fig. 2. Structure of Cured Novalac with Hexamethylenetetramine.

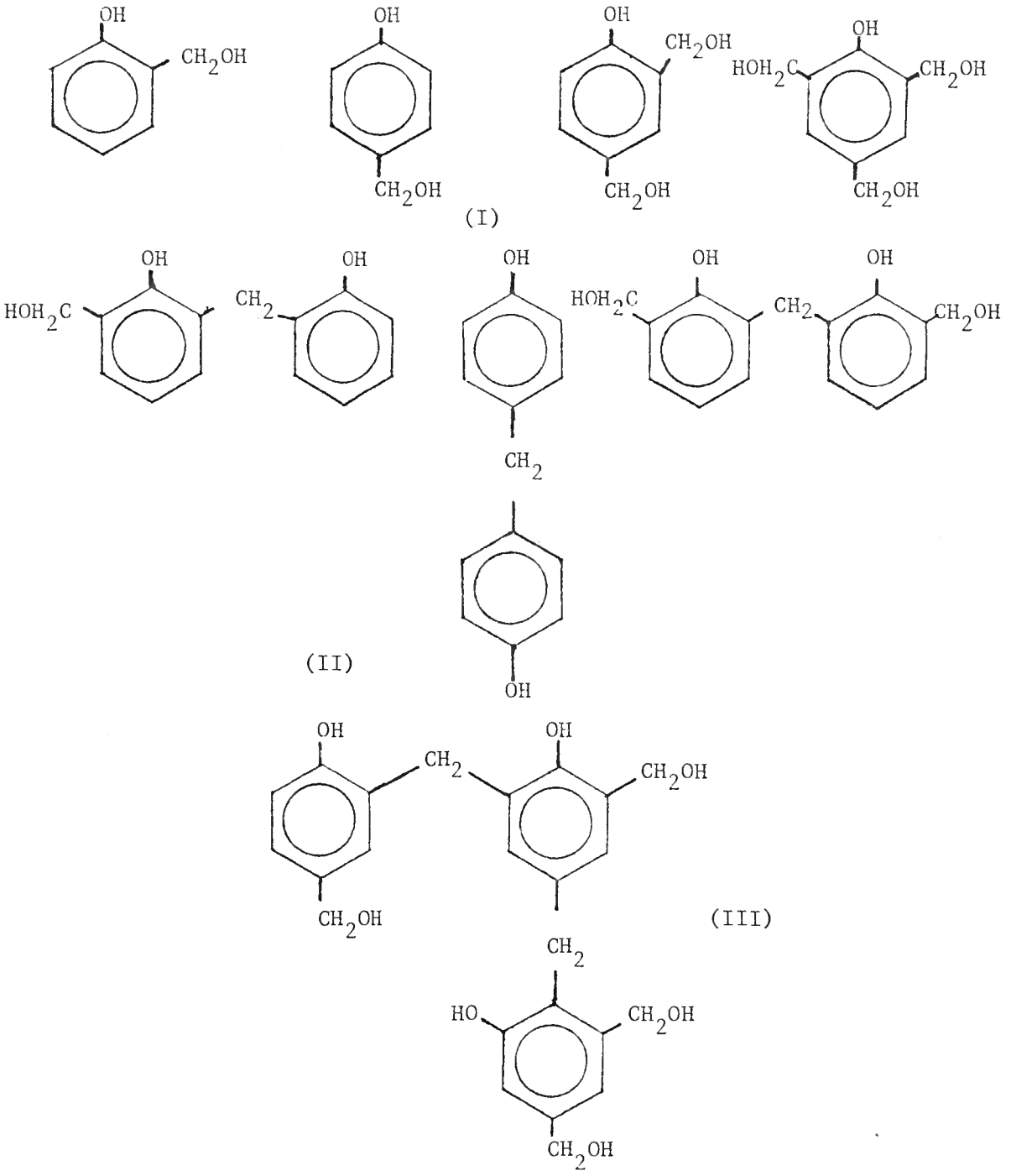


Fig. 3. Resole Prepolymers.

two-step resins proceed from a low-molecular weight resin to a resin with molecular weights as high as 10,000. Two-step resins are cured by the addition of "hexa" with an increase in temperature and the formation of a three-dimensional structure. One-step resins can be cured simply by the addition of heat. Curing in each process occurs by the formation of methylene and methylene ether linkages. Ether formation occurs with highly methylated phenols at temperatures of 130°C or below or when other reactive positions are blocked as in alkylphenols.[21] These results are substantiated by Lilley, who showed the formation of bridges depends on the distribution of activation in the molecules of phenol alcohol.[22]

The three-dimensional structure of a cured resin is highly rigid (Fig. 4). It is because of this inflexable structure that they are unreactive to heat and most solvents.

To substantiate the production of a potentially useful resin, characterization of the polymer is performed by using differential thermal analysis (DTA). This technique measures the temperature of a sample and a thermally inert reference material as they are heated. Any transition which the sample undergoes will result in the liberation or absorption of energy by the sample with a corresponding deviation of its temperature from that of the reference.[17] DTA measurements used for thermal work in this study were carried out using a differential thermal analysis cell with a DSG (Differential Scanning Calorimetry) program mode. This method is very closely related to DTA by the fact that the sample and reference materials are also monitored for thermal transitions that may occur during heating or cooling. However, in this method, if a transition occurs in the sample, thermal energy is added or subtracted from the sample or

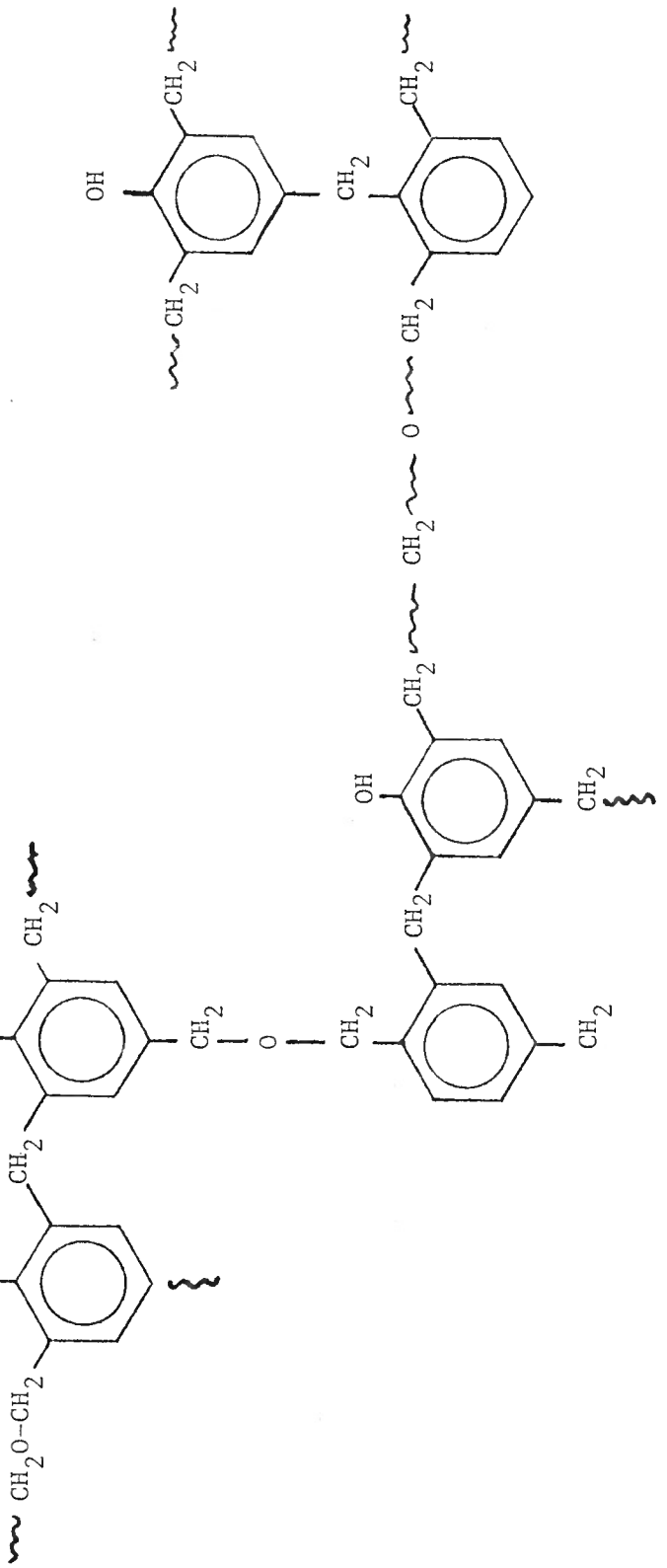


Fig. 4. Structure of Cured Resole Resin.

reference containers in order to maintain both sample and reference at the same temperature.[18] Therefore, direct calorimetric measurement of the transition energy can be obtained from the amount of energy put in or taken out corresponding to the energy that is given off or absorbed. A schematic in Figure 5 represents a typical DTA cell. Thermograms taken from measurements of polymeric samples will give a number of endotherms and exotherms from which a qualitative identification can be made of the type of polymer formed, extent of polymerization, range of molecular weight, and temperature of cure.

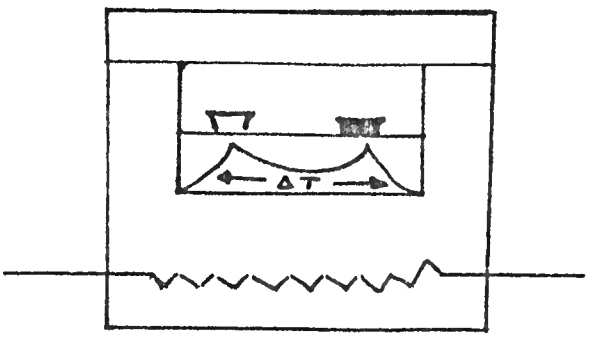


Fig. 5. Single Heat Source DTA Cell.

Solubilities, as discussed above, give a good indication of the stage of polymerization the polymer product has reached. Low molecular weight, a-stage resoles are soluble in most organic solvents and sometimes water. With the advent of further condensation, the molecular weight increases and the solubility of the product decreases as the b-stage resitol resin is reached. Finally, insoluble c-stage resites are reached upon careful

dehydration of resin to the network thermoset. Molecular weights of resoles are usually within the 300-700 range and the molecular weight may be determined by the Rast method. This method involves the determination of the melting point depression of a pure solvent when a soluble sample is added. This approach can be used for an approximation of the number-average molecular weight ($\overline{M}_n$).

Infrared analysis can be used for identifying the stretching and bending modes of certain functional groups specific to reactants and products. As electromagnetic radiation passes through molecules, the energy is transmitted, scattered and absorbed.[19] The relationship existing between the wavelength of the absorbed light and the structure of the molecules make infrared spectroscopy a useful and fast method of analysis. In analyzing phenolic resins, there are a variety of functional groups from different but similar compounds which overlap in their absorption. This makes identification of weak and medium absorbing functional groups difficult but possible. The strongly absorbing functional groups are readily recognized and because of their presence in these complex resin mixtures, the spectra obtained have a uniqueness related only to phenolic resins.

It is the intent of this thesis to give an accurate account of (1) the development of a method of separation of phenols from the pyrolytic oils, (2) the production of a high molecular weight product using the extracted phenols from pyrolytic oils, and (3) the characterization of the final resinous material by determination of solubilities in organic solvents, the molecular weight, melting point, infrared spectra analysis, and differential thermal analysis.

The problem which this thesis will address will be the feasibility of extracting phenols from pyrolytic oil for use as precursors for the production of a thermosetting resin. If we can prove the utility of the oils for yielding phenols and other derivatives, this will then offer another working alternative for their production and subsequent use.

RESULTS AND DISCUSSION

Extraction Procedures

This study involved developing an effective separation scheme for the pyrolytic oils that would yield a product which could be used to produce a fairly high molecular weight resin. This resin could be further cured by heat to obtain a three-dimensional thermosetting resin. It would be of high molecular weight, infusible and impenetrable to solvent molecules. The use of solvent extraction techniques offers a greater flexibility than most other separation systems. It is relatively inexpensive; requires no unusual equipment; recovery of product is simple; product is usually easily purified and obtained in sufficient quantity, and expeditiously. Finding the correct combination of solubility relationships to produce a feasible separation method was the major problem. Through the procedures described in this study, a workable system of separation was eventually proposed.

This was successfully done using the separation scheme presented in procedure (A) in the experimental section of this thesis. The extraction procedures are performed in a separating funnel and are diagramed schematically below (Fig. 6). In the first extraction with water, low molecular weight polar materials (ROH, RCHO, RCO_2R, $RCONH_2$) are usually removed at room temperature. In fact, the pyrolytic oils contain a variety of low molecular weight alcohols, aldehydes, ketones, and acids as reported in Table 1. The next step involved the use of a weak base. Carboxylic acids and other strong acids will react with weak bases such

as $NaHCO_3$. Therefore, it was assumed that the soluble layer contained salts of strong acids such as carboxylic acids and also some phenols, with electron withdrawing groups. However, most weak acids, in particular phenols, are insoluble in weak bases but quite soluble in a strong base such as sodium hydroxide solution. Next sodium hydroxide solution converts phenols to their corresponding salts which are soluble in water and insoluble in organic solvents, such as ethers. Therefore, HCl is added to convert these salts to their original form to be extracted by ether.

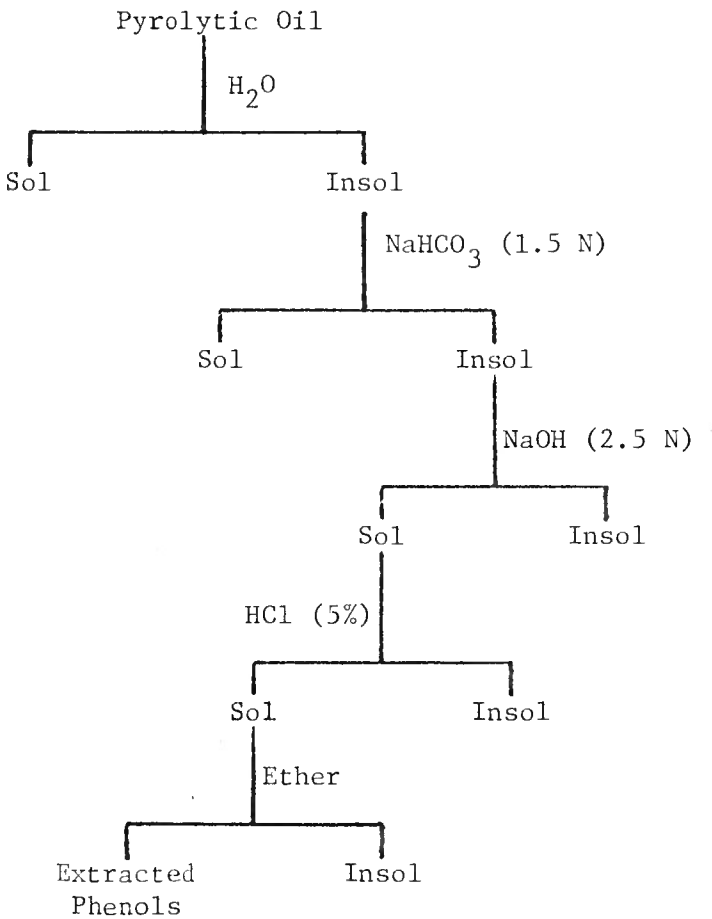


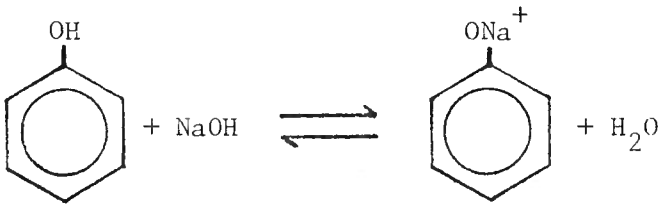
Fig. 6. Extraction Procedures.

Table 1. Compounds Which Have Been Identified And Reported in the Literature as Being among the Products of Wood Distillation.*

Formic acid	Acetone	Dimethyl ether of methyl pyrogallol
Acetic acid	Methyl ethyl ketone	
Propionic acid	Diethyl ketone	Dimethyl ether of propyl pyrogallol
Burytic acid	Methyl propyl ketone	Creosol
Valeric acid	Methyl butyl ketone	Eugenol
Caproic acid	Ethyl propyl ketone	
Crotonic acid	Cyclopentanone	Ammonia
Angelic acid	Methyl cyclopentanone	Methyl amine
Pyromucic acid	Adipic ketone	Pyridine
Lignoceric acid	Diacetyl	Methyl pyridine
Valerolacetone		
	Phenol	Pyroxanthone
Methyl alcohol	o-, m-, and p-cresol	Methylal
Allyl alcohol	Phlorol	Dimethyl acetal
Isoamyl alcohol	1,3 xylenol-5	
Isobutyl alcohol	Pyrocatechol	Dimethyl furane
3-Butenol-2	Guaiacol	Trimethyl furane
	Ethyl guaiacol	Sylvane
Formaldehyde	Dimethyl ether of homopyrocatechol	α,α'-dimethyl tetrahydrofurane
Acetaldehyde	Coerolignol	α-methyl-α'ethyl α,β'-dihydrofurane
Valeric aldehyde	Pyrogallol	m-xylene
Furfural	Dimethyl ether of pyrogallol	Toluene
Methyl furfural		Melene $C_{30}H_{60}$

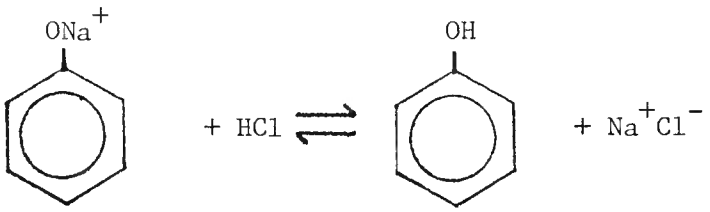
*Hawley, L. F. and Wise, L. E., "The Chemistry of Wood," Chemical Catalog Co., Inc. (1926).

In the separation of dissolved weak acids from the aqueous layer, it is assumed that the equilibrium represented by equation 1 is present after extracting with the sodium hydroxide solution.



(1)

Dissolved salts of acids are quite soluble in the aqueous medium and insoluble in organic solvents. Conversion of these salts to their acid form was done by acidifying with hydrochloric acid. Equation 2 is a representation of the reaction by which the acid form becomes extractable with ether.



(2)

After this extraction, each of the ether-pyrolytic oil extracts was rotary evaporated. The sample recovered was analyzed using capillary gas chromatographic techniques.

The results obtained were very significant. In comparing the chromatogram of the phenol extract with that obtained for an uncut sample of pyrolytic oil, most peaks relating to phenols and derivatives were in complete agreement. The uncut sample of pyrolytic oil was a distilled product analyzed by capillary gas chromatography with many of

the peaks identified by peak enhancement studies. Figure 7 and Table 2 show the results from that analysis which confirmed the presence of phenolic compounds capable of producing a suitable resin.

The procedures which led to this final method of extracting phenols were of great significance, also. Procedure (B) describes a basic outline contained in an EPA progress report concerning a method for stabilization of pyrolytic oils.[23] This method involved a separation procedure similar to the one described above. Extraction of the mixture with water followed by the addition of a 5% sodium hydroxide solution which solubilized the insoluble fraction and extraction with ether produced a homogeneous mixture. The ether and (aq) sodium hydroxide phases were indistinguishable. This was tried several times with the same results, and was modified to give procedure (C). The problems with this procedure resulted from working with the insoluble fraction after extracting with aqueous hydroxide solution. Treatment of the insoluble fraction after the water extraction with NaOH should have converted most of the strong and weak acids to their corresponding sodium salts. These salts would be quite soluble and thus contained in the aqueous layer. Most of the high molecular weight ethers would be insoluble. The insoluble fraction was further extracted with sodium bicarbonate solution followed by ether extraction. Also the aqueous layer was extracted with ether. The infrared spectra of the two extracts were quite similar. The results are reported for the two in Table 3 There was a weak aromatic -C-H stretch at 3000 cm^{-1}. Also, there were indications of small amounts of ethers present from the intense absorption of -C-O at 1045 cm^{-1} (indicative of ethers). These spectra did not give a definitive

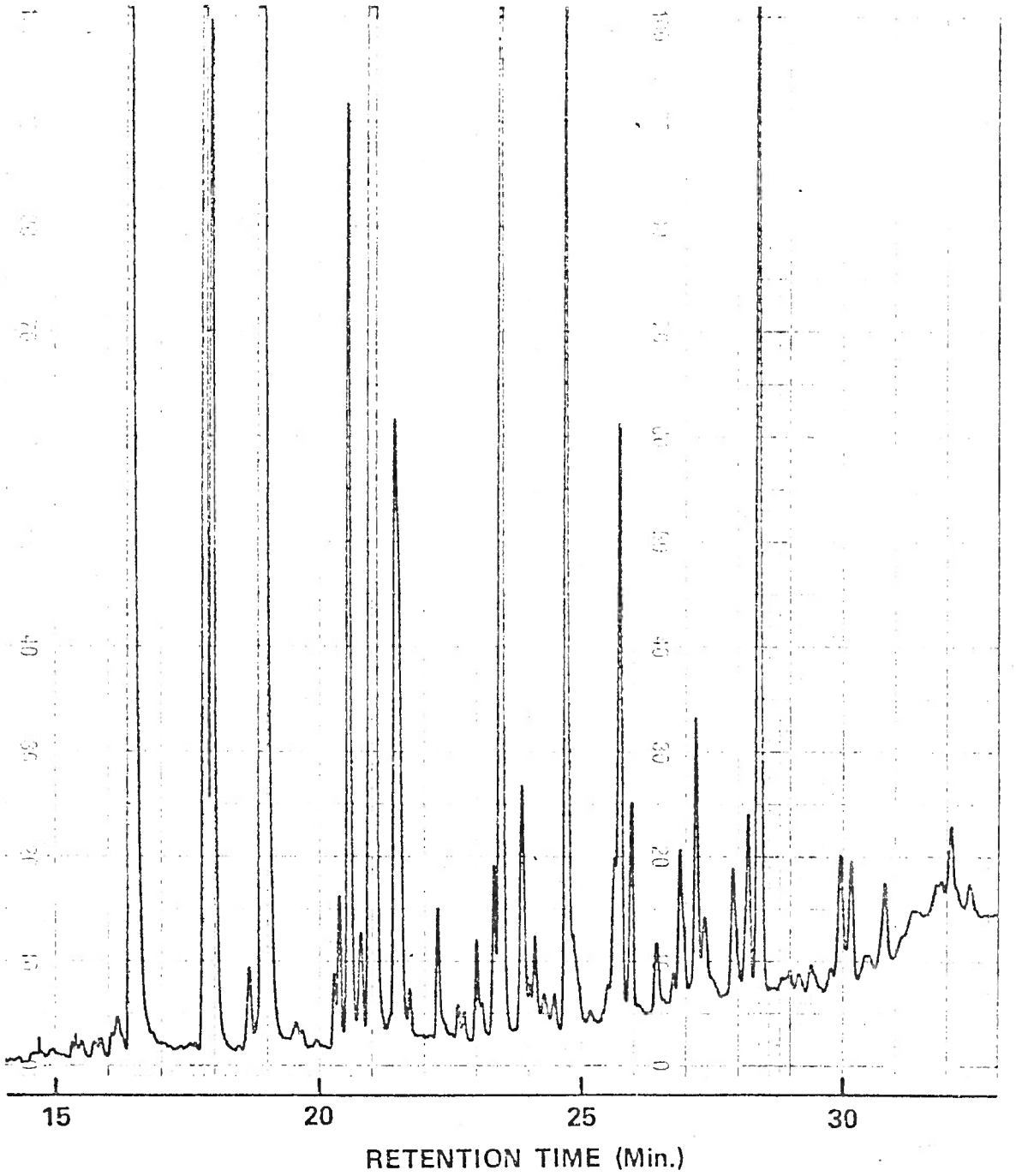


Figure 7. Capillary Gas Chromatogram of Phenolic Extract.

Table 2. Peak Assignments.

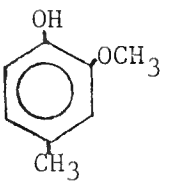
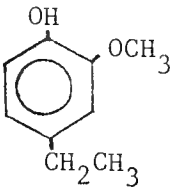
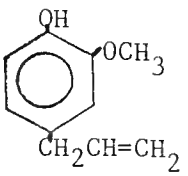
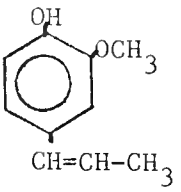
Retention Time (Min)	Assignment
16.40	Phenol
17.80	Guaiacol
18.00	o-Cresol
19.00	m- and p-Cresol
21.00	
23.40	
24.70	 (Eugenol)
28.40	 (Isoeugenol)

Table 3. Infrared Analysis of Phenolic Extract C.

Intensity	Group Assignment	Wave Number
Strong, Broad	OH- Stretch	3500-3490 cm^{-1}
Weak, Aromatic	-C-H Stretch	3010 cm^{-1}
Strong, Sharp	Sat'd -C-H Stretch	2900 cm^{-1}
Strong	>C=O Stretch	1710 cm^{-1}
Medium, Sharp	>C=C< Stretch	1610 cm^{-1} and 1520 cm^{-1}
Strong	-C-O Stretch	1275 cm^{-1}
Medium, Sharp	-C-O Stretch	1045 cm^{-1}

indication of the presence of phenols or derivatives that could be used in the polymerization process.

Procedure (D) gave the infrared results reported in Table 4. Here, also, a very close similarity was noted in the spectra as well as the procedures. The main differences were the direct use of NaOH instead of first extracting with water, followed by the addition of HCl. The idea was to first convert all the soluble materials to their salts because some phenols are soluble in water. Procedure (E) led to the infrared results reported in Table 5. Each procedure thus far used had very similar functional group absorption characteristics. However, this procedure gave fractions with clearly identifiable aromatic character present with the ortho-disubstitution pattern noted at 810 cm^{-1}. Also noted was the fact that upon addition of the sodium hydroxide solution, the pyrolytic oil samples became increasingly more soluble. At the start of these procedures, sodium hydroxide produced a soluble and insoluble layer, but as the procedures were modified during the course of this study, most of the components became quite soluble.

Procedure (F) was based on the principle of effecting separation of the phenols through extraction with water at various temperatures. Phenols are somewhat soluble in water (about 9.2 grams per 100 grams of water at room temperature for phenol itself). Also, o-, m-, and p-cresols are soluble to 2.5, 2.6, and 2.3 grams per 100 grams of water at 25°C, respectively.[24] By increasing the temperature of the water used for extraction, there should be an increase in their solubilities. The infrared results reported in Table 6 show better resolution of the functional group absorption. Aromatic -C-H stretches are quite clear

Table 4. Infrared Analysis of Phenolic Extract D.

Intensity	Group Assignment	Wave Number
strong, broad	OH- Stretch	3580 - 3500 cm^{-1}
weak, aromatic	-CH Stretch	3060 cm^{-1}
strong, broad	Sat'd -C-H Stretch	2980 - 2920 cm^{-1}
strong	$\backslash C{=}O$ Stretch	1720 cm^{-1}
medium	$\backslash C{=}C\ /$ Stretch	1620 cm^{-1} or 1520 cm^{-1}
strong, broad	-C-O Stretch	1280 - 1260 cm^{-1}
medium, sharp	-C-O Stretch	1040 cm^{-1}

Table 5. Infrared Analysis of Phenolic Extract E.

Intensity	Group Assignment	Wave Number
strong, broad	OH- Stretch	3470 - 3300 cm^{-1}
strong, broad	Sat'd -C-H Stretch	3070 cm^{-1}
strong, broad	$\backslash C{=}O$ Stretch	1720 - 1680 cm^{-1}
strong	$\backslash C{=}C\backslash$ Stretch	1600 cm^{-1} or 1510 cm^{-1}
strong	-C-O Stretch	1230 cm^{-1}
strong	-C-O Stretch Aromatic Ketones	1035 cm^{-1}
strong	Ortho di-subst	810 cm^{-1}
weak	Aromatic -C-H Stretch	3070 cm^{-1}

Table 6. Infrared Analysis of Phenolic Extract F.

Intensity	Group Assignment	Wave Number
strong, broad	OH- Stretch	3440 - 3220 cm^{-1}
medium, aromatic	-CH- Stretch	3060 cm^{-1}
medium, broad	-C-H Stretch	2965 - 2920 cm^{-1}
strong, intense	$\backslash C{=}O$ Stretch	1710 cm^{-1}
medium	$\backslash C{=}C\ /$ Stretch	1600 cm^{-1} and 1510 cm^{-1}
medium, sharp	OH- Bending	1400 cm^{-1}
medium	-C-O Stretch	1095 cm^{-1}
strong	-C-O Stretch	1380 cm^{-1}
medium	di-substitution pattern	880, 850, 810 cm^{-1}

at 3060 cm^{-1}. A strongly absorbing carbonyl, possibly an aldehyde or ketone, was detected. Also detected were sharp absorption peaks at 1380 and 1095 cm^{-1} corresponding to -C-O functional groups. These results were highly reproducible for each extraction obtained. However, there was still the presence of a strongly absorbing carbonyl group in each spectrum. The absence of carbonyl absorption was used as a measure of the success of the separation procedure. Also, GC/MS data were obtained for this extraction, and Fig. 8 and Table 7 describe the results obtained. The interpretation of the GC/MS data was carried out by the study of the fragmentation patterns in the mass spectra and comparing the peaks with mass spectral data compiled in the literature, and research previously done by other project researchers.[25] The fragmentation pattern of the phenols are reported in Figures 9-12. This spectral data clearly shows the presence of phenolic compounds along with alcohols and acids. This correlates with the solubilities of these compounds which as low molecular weight alcohols and acids should be soluble in addition to the weakly acidic phenols in water.

Procedure (G) developed from the approach of using elevated temperatures for extracting with water. This method possibly resulted in a better removal of water soluble compounds, because the infrared results showed little or no carbonyl absorption (Table 8). However, the results were not reproducible. Only a dark liquid layer formed, and the infrared spectrum showed strong carbonyl absorption. The insoluble solid that was isolated in the procedure formed a very oily mass and could not be dried to run a KBr pellet. However, the infrared spectra were very similar to those reported in procedure (D) from portions dissolved in methylene chloride.

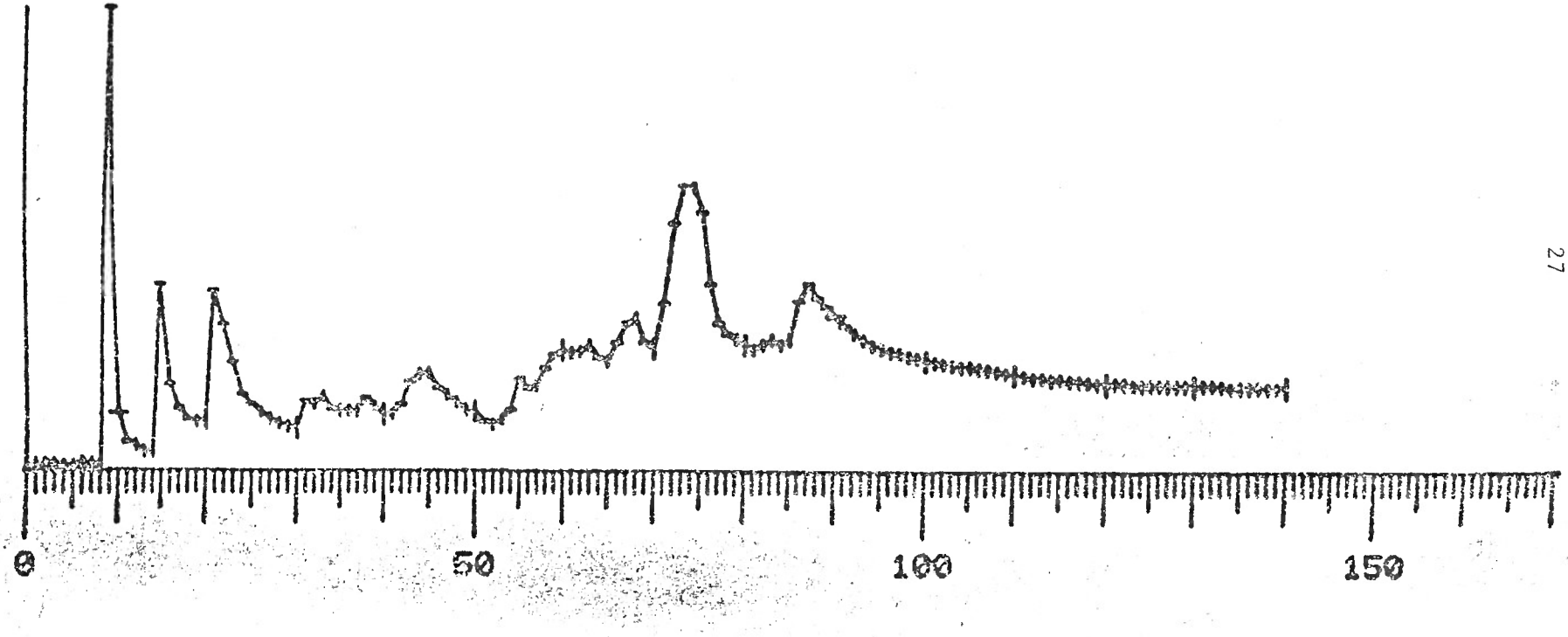


Fig. 8. Gas Chromatogram of Phenol Extract at 60°C.

Table 7. Statistical Data of GC/MS Run.

Peak Number	Area %	Retention Time	Area
1	.001	14	27
2	.002	18	54
3	6.034	67	187011
4	1.641	115	50854
5	3.066	157	95018
6	1.033	241	32088
7	1.152	277	35716
9	4.236	426	131267
10	2.319	453	71867
11	4.733	487	146680
12	10.75	525	333252
13	2.656	567	82331
14	6.782	617	210175
15	5.319	634	164828
16	2.765	686	85706
17	12.84	775	397939
18	7.854	825	243429
19	6.466	854	200395
20	5.315	894	164717
21	5.35	930	165816
22	4.487	987	139063
23	2.713	1014	84095
TOTALS	100		3100470

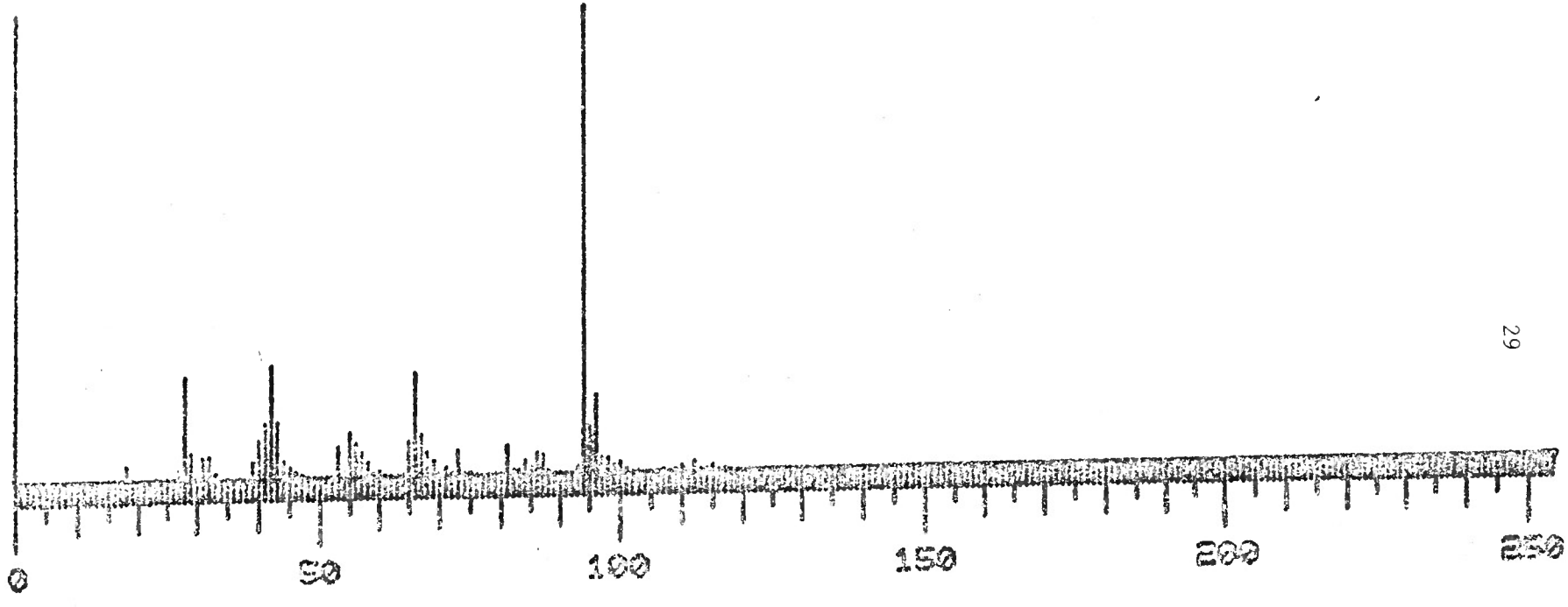


Fig. 9. Mass Spectrum of Phenol.

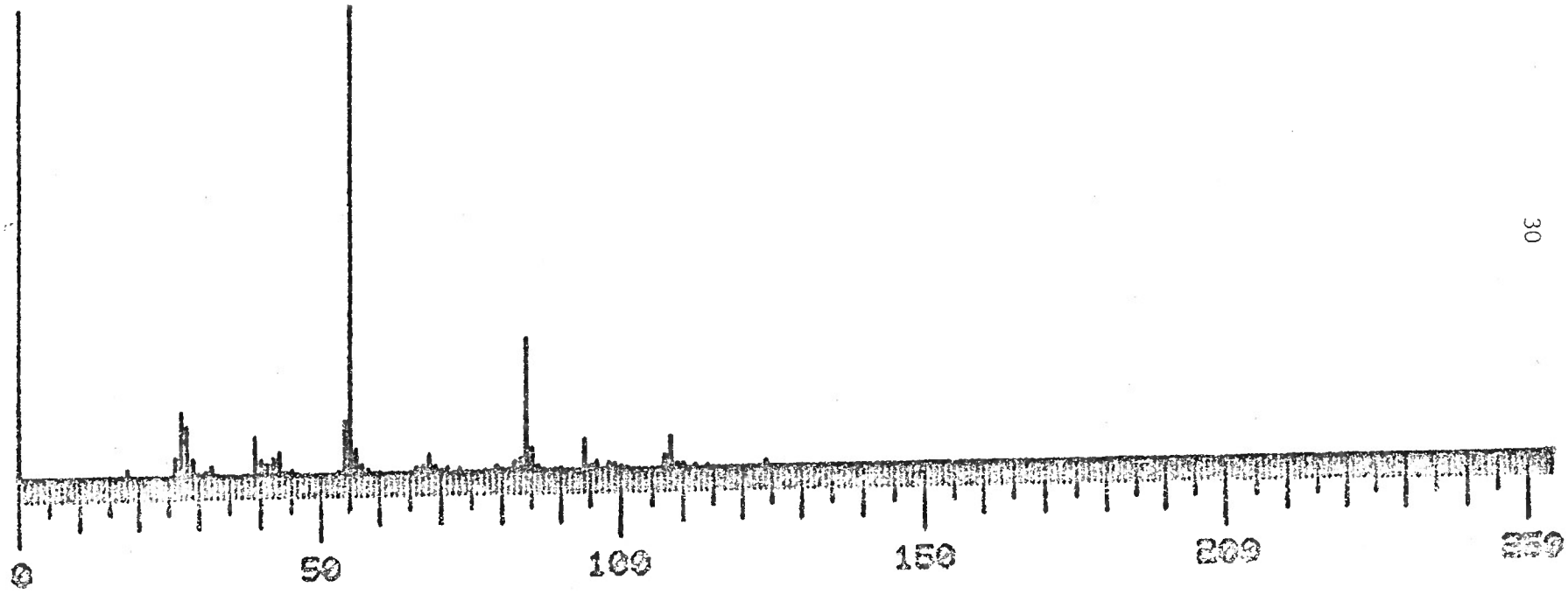


Fig. 10. Mass Spectrum of Cresol.

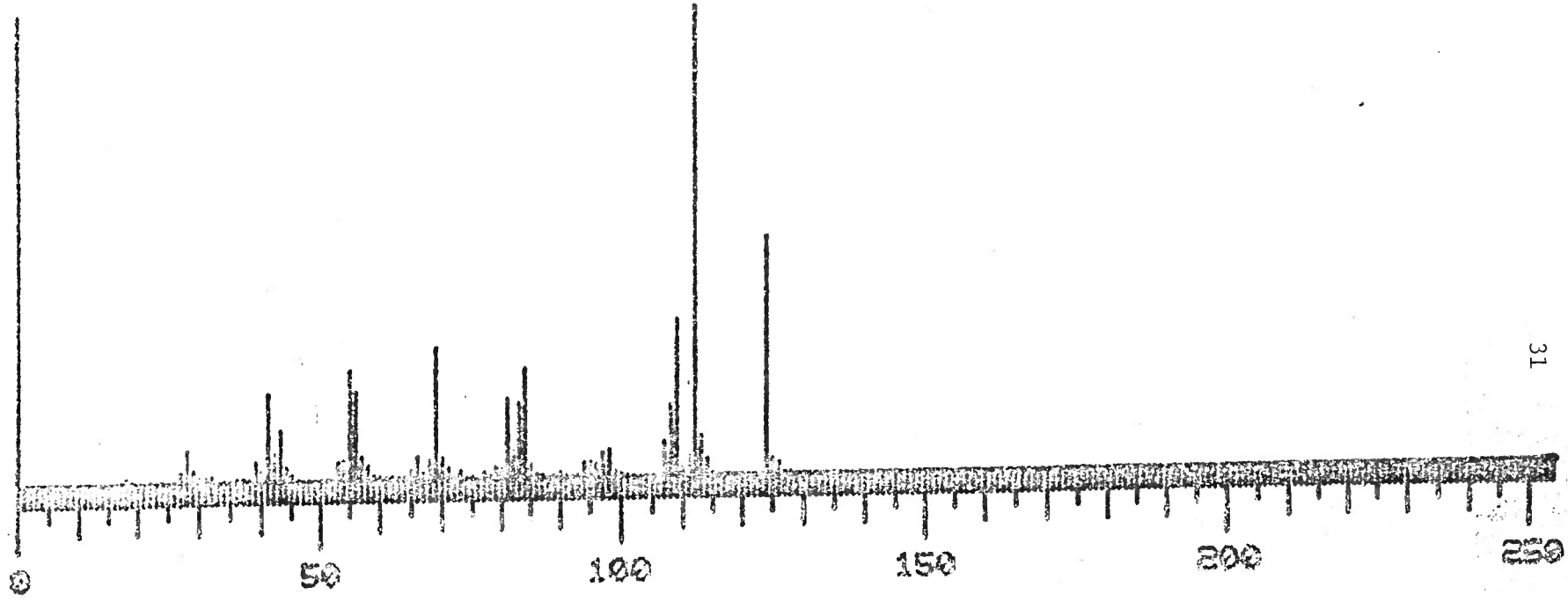


Fig. 11. Mass Spectrum of Cresol and Guaiacol.

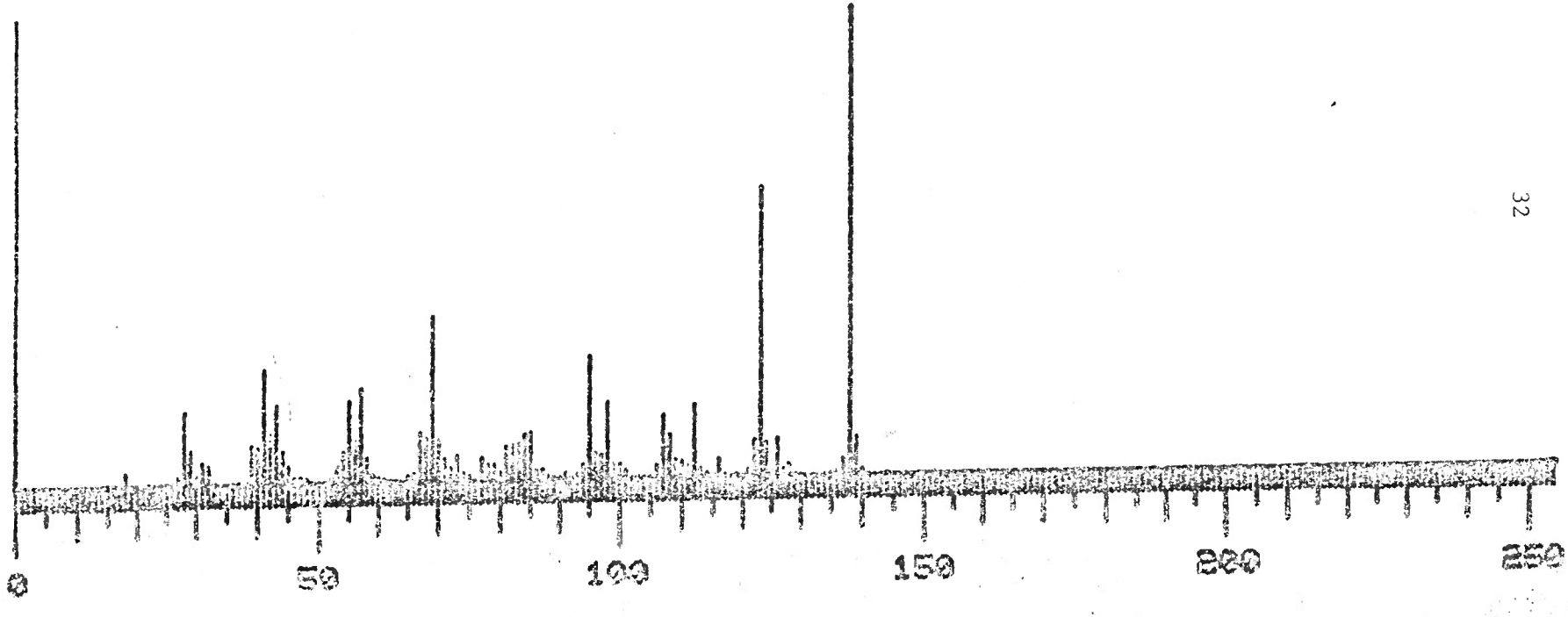


Fig. 12. Mass Spectrum of 2-Methoxy-4-Methyl Phenol.

Table 8. Infrared Analysis of Phenolic Extract G.

Intensity	Group Assignment	Wave Number
strong, broad	-OH Stretch	3480 - 3260 cm^{-1}
medium	-C-H Sat'd Stretch	2920 cm^{-1}
strong	$\diagdown C{=}C \diagup$ Stretch	1565 cm^{-1}
medium	OH Bend	1400 cm^{-1}
medium (Intense)	Mono Substitution	840 cm^{-1}

Polymerization Studies

The polymerization of m-cresol served as a model for preparing resole resins. Since phenol has a functionality of three and formaldehyde a functionality of two, these compounds can condense to form a three-dimensional resin. However, the reactive prsitions are the two ortho and one para position on the phenol ring. The meta positions will not react under normal conditions and are thus considered inactive.[26] Functionality refers to the number of reactive positions or functional groups, and it determines the type of resin produced. If ortho or para-alkyl substituted phenols are reacted, they only have the functionality to produce linear polymers. Ortho and para-cresols are bifunctional and form only linear polymers, whereas m-cresol is tri-functional. Thus it can be reacted to form a three dimensional thermoset.

Reagent grade m-cresol and formalin (37% formaldehyde) were reacted together in the presence of ammonia to form a very brittle resinous material. This material was a dull yellowish color and could be dissolved in acetone. The infrared analysis is reported in Table 9. The results show the broad characteristic -OH absorbance at 3340 - 3260 cm^{-1}, and the -OH bending mode at 1270 cm^{-1}.

Polymerization of the extracted phenols led to similar results. In this procedure, barium hydroxide was used as the alkaline catalyst and the mixture of extracted phenols were reacted with formaldehyde in a 1:2.5 molar ratio, respectively. If the reaction mixture contains less than one mole of formaldehyde per mole of phenol it has sufficient functionality but not enough crosslinking ingredient to form a thermosetting resin and a thermoplastic will result.[27] The reaction

Table 9. Infrared Analysis of Resole Polymer from Shelf Reagents.

Intensity	Group Assignment	Wave Number
strong, broad	-OH Stretch	3340 - 3260 cm^{-1}
medium	Aliphatic C-H Stretch	2890 cm^{-1}
strong	 Stretch	1580 cm^{-1}
strong, broad	OH Bending	1435 - 1535 cm^{-1}
strong	-C-O Stretch	1270 cm^{-1}
medium	disubstitution pattern	850 - 800 cm^{-1}

was maintained at 70°C while stirring and this is termed the first phase of polymerization. In the second phase, the mixture contained in the reaction pot was neutralized with oxalic acid to a pH of about 6-7 using pH paper to determine the point of neutralization. Water was then removed by distillation under reduced pressure. At 15 minute intervals, 1-2 ml samples from the resin kettle were taken to check the extent of condensation. As the samples became more and more viscous, the reaction was terminated as the material began to solidify and become non-tacky.

Characterization of the resinous product was carried out by solubility tests, differential thermal analysis, melting point determination, molecular weight determination, and infrared analysis.

Solubility characterization can give good information about the stage of polymerization and the overall molecular weight of the resin. As the molecular weight increases, solubility decreases with the formation of more and more methylene ether bridges and methylene bridges. Resole or a-stage resins are soluble in alcohols, esters, ketones, phenols and some ethers, and insoluble in hydrocarbon oils.[28] In testing the solubility of the polymeric materials, it was found that ethyl and methyl alcohol, formic acid, and (bez) benzene had no solubilizing effect on the resin. However, acetone and phenol were quite effective, and gave good indication that the polymer produced was a b-stage resitol. The resitol polymers have slightly higher molecular weights than the resols, due to the greater extent of condensation. This is in good agreement with the experiment performed since the reaction was carried beyond the point for resole polymers

for differential thermal analysis purposes. The resitol polymers only differ slightly in physical characteristics and are chemically formed by the same procedure. All polymers formed from an alkaline catalyst and an excess of formaldehyde are generally termed resoles.

When the resin was dissolved in acetone, a white precipitate was formed. This precipitate was tested for solubility in benzene, alcohol, aqueous acids, phenol, and formic acid. None of the solvents used showed any effect on the precipitate, and the infrared results reported in Table 10 were then studied for absorption of specific functional groups. The infrared analysis gave a good indication that the white filtrate may be of polymeric nature. This may have resulted from a side reaction which occurred during the polymerization in which this material was a minor product. The material had no visually observable melting point, but the DTA thermogram obtained showed a series of endotherms corresponding to melting point transitions. These endotherms occurred in a temperature range of 85-175^{o}C which is quite indicative of non-linear, branched chain polymers.[29] This white filtrate could have resulted from the polymerization of some of the ortho-, para-alkyl substituted components in the pyrolytic oils, possibly from the polymerization of eugenol or isoeugenol. However, this material was not the material needed for this particular study of the pyrolytic oils. Thermograms of the white filtrate are shown in Figs. 13 and 14. The first thermogram shows the series of melting transitions and the second thermogram represents a DSC analysis of the product from the first run in which no peaks are present since this material was in the cross-linked state induced by the heating in the first run.

Table 10. Infrared Analysis of White Filtrate.

Intensity	Group Assignment	Wave Number
strong, broad	-OH Stretch	3425 - 3320 cm^{-1}
weak, sharp	-C-H Stretch	2910 cm^{-1}
weak	$\backslash C{=}O$ Stretch	1710 cm^{-1}
strong	$C{=}C$ Stretch	1610 cm^{-1}
weak, broad	-OH Bending	1400 cm^{-1}
strong, sharp	-C-O Stretch	1310 cm^{-1}
medium, sharp	$-CH_2-$ Stretch	775 cm^{-1}
strong	disubstituted Stretch	710 cm^{-1}

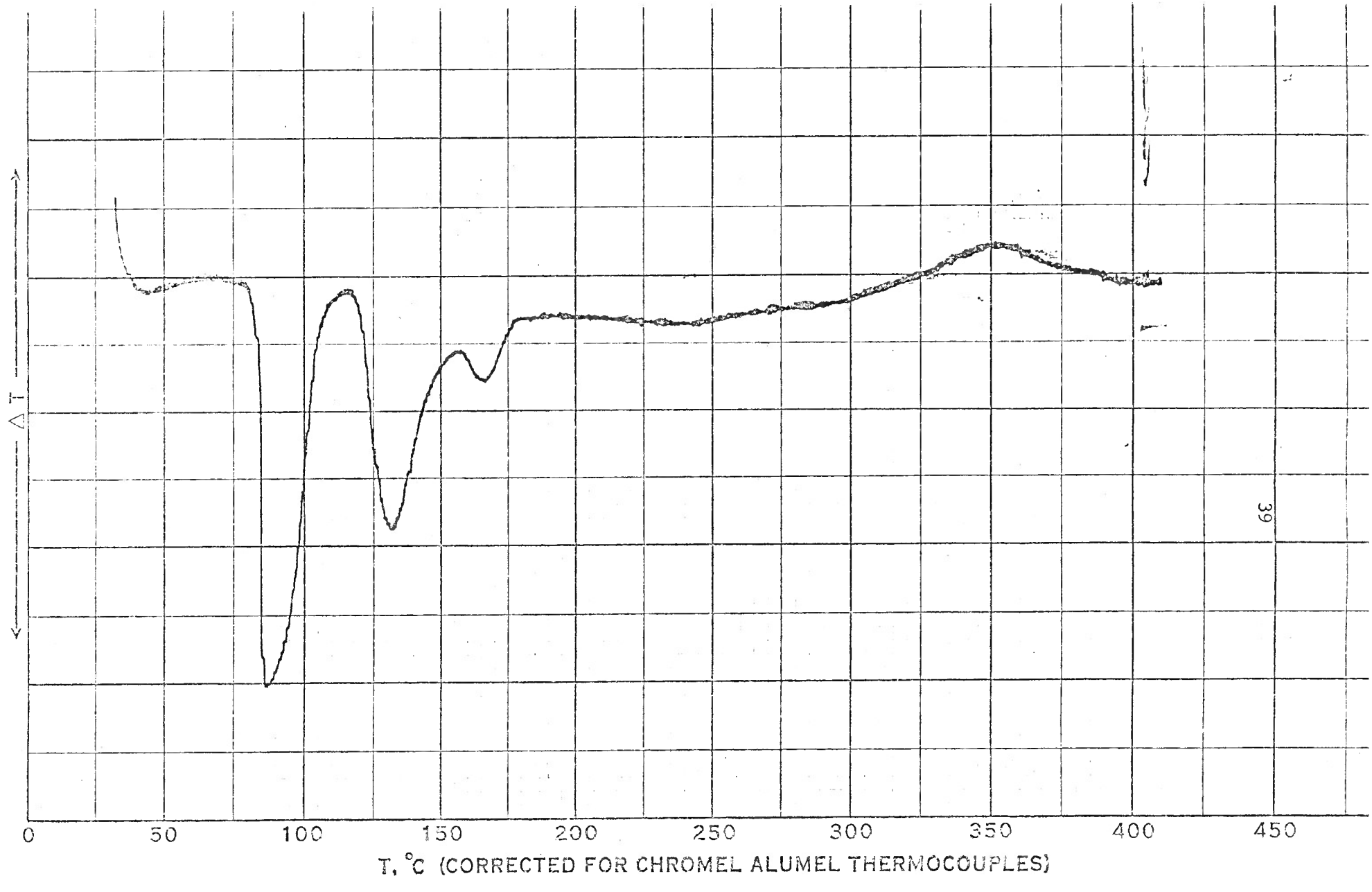


Fig. 13. Thermogram of White Filtrate - First Run.

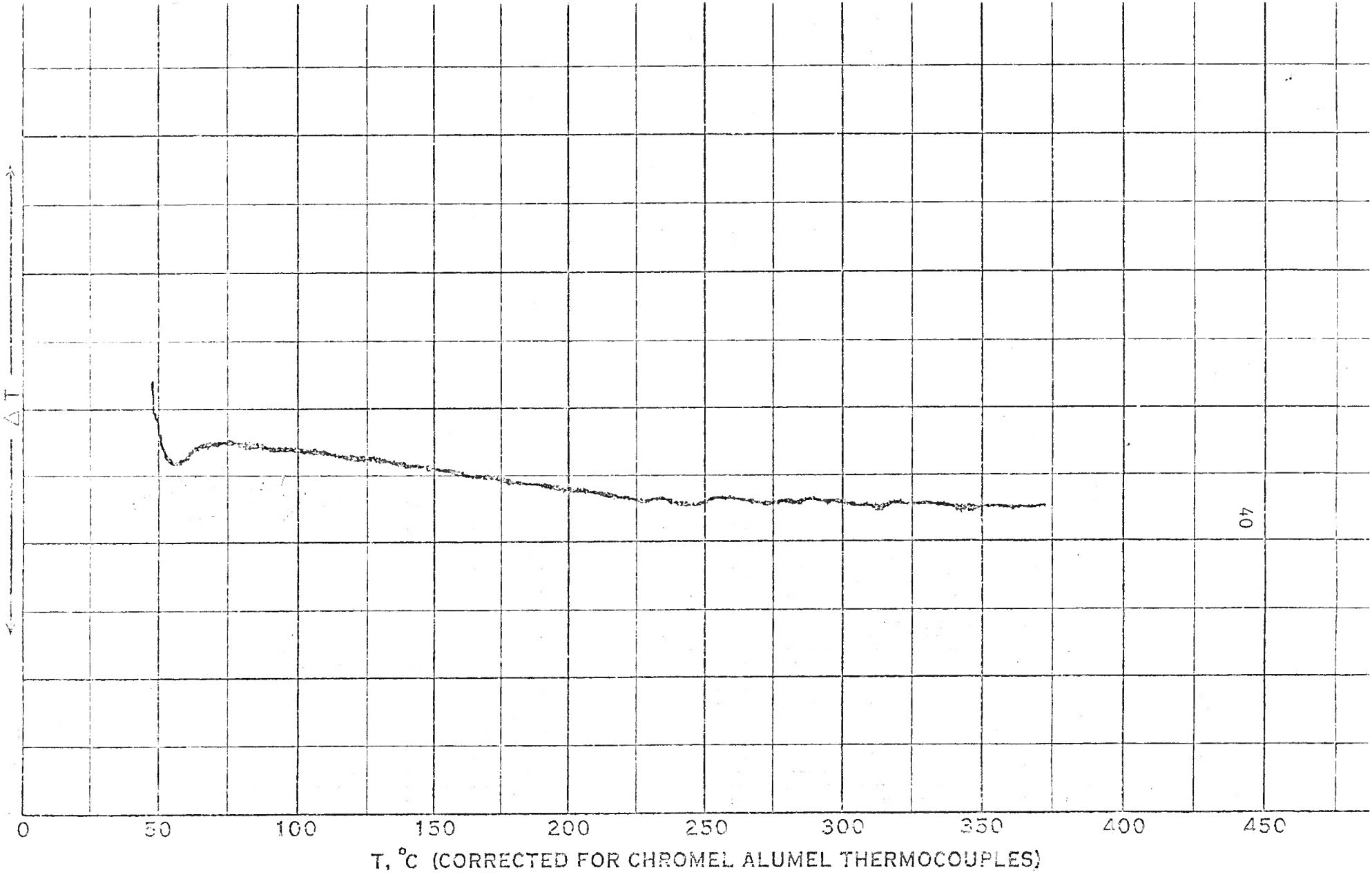


Fig. 14. Thermogram of White Filtrate - Second Run.

Since this material did not dissolve in any of the solvents tried, a molecular weight determination was not possible. The acetone solution was evaporated to obtain a brown grindable solid which dissolved in phenol. A melting point determination gave a rather broad melting point range which was verified by differential thermal analysis. The thermogram showed a glass transition temperature (Tg) of 105°C, a crystallization exotherm at 360°C, and a crystalline melting point of 400°C (Fig. 15). DSC is very sensitive to any physical and chemical transitions which may occur during heating; therefore, precise thermal transitions can be detected and recorded. Also, an infrared spectrum of the final resin was obtained and the results are reported in Table 11 and Fig. 16. The results agreed with peak assignments by Kagarise and Weinberger[30] and also Bellamy [31] for phenol and methylol groups. The bending mode for hydroxyl groups in methylol structures ($-CH_2-OH$) was present, but may have been masked by overlapping of many other groups. The strong absorption at 1250-1200 cm^{-1} was indicative of phenolic -OH bending which may arise from free phenolic groups present in the reaction mixture. In a report by Katovic[32] concerning thermal analysis of cured phenol resins, it was mentioned that curing of resins could be followed by infrared analysis. This was done by monitoring the disappearance and appearance of certain absorption frequencies corresponding to reactive functional groups, i.e., the disappearance of the frequency corresponding to the bending of -C-O-C- groups of methylene ether linkages.

The extracts taken from the reaction process were also analyzed by DTA immediately following their extraction from the reaction mixture.

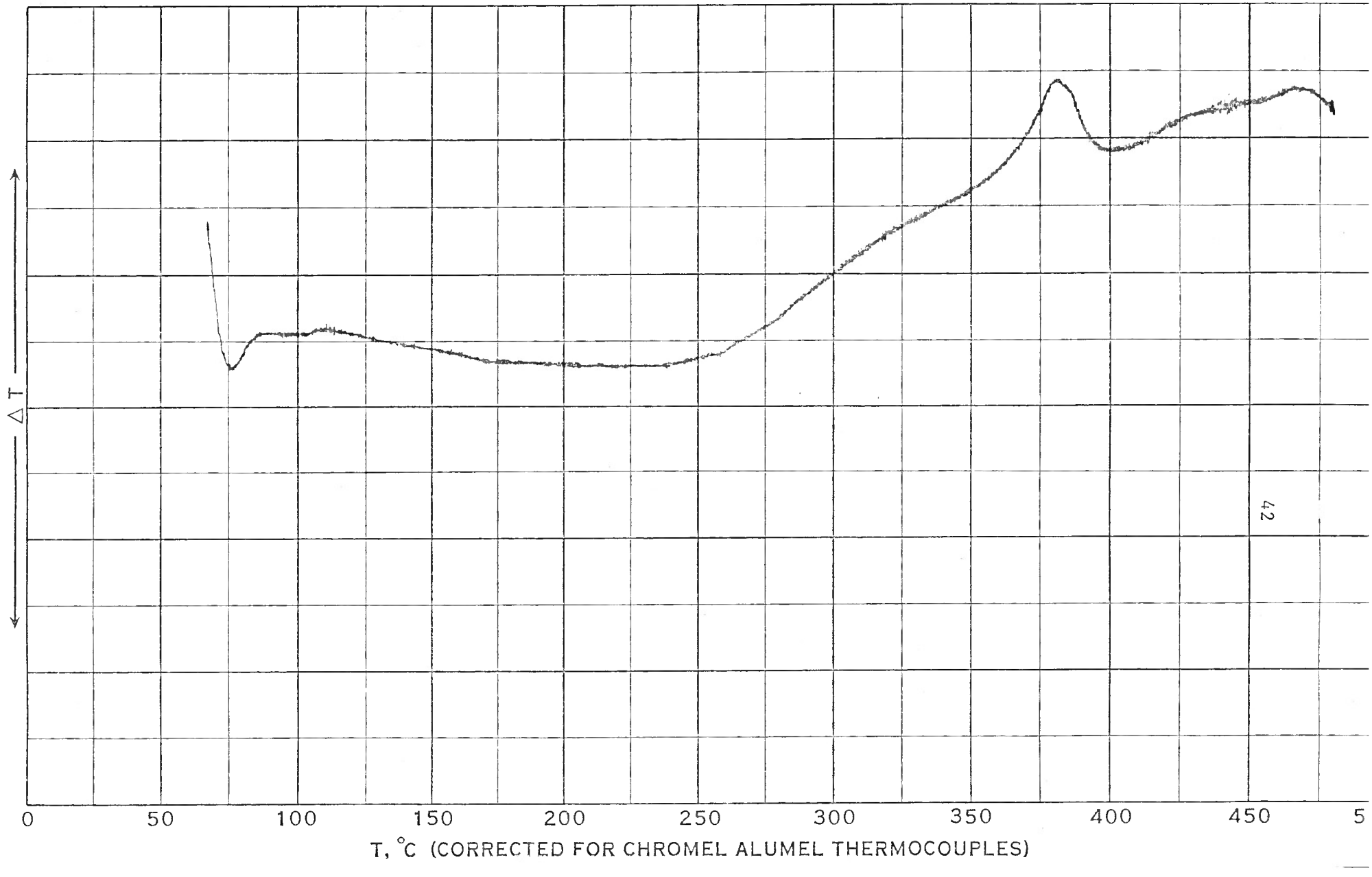


Fig. 15. Thermogram of Brown Polymeric Material.

Table 11. Brown Solid. Infrared Analysis of Extracted Resole Resin.

Intensity	Group Assignment	Wave Number
strong, broad	-OH Stretch	3485 - 3320 cm^{-1}
strong, sharp	-C-H Stretch	2930 cm^{-1}
weak	$\backslash C{=}O$ Stretch	1700 cm^{-1}
strong	$C{=}C$ Stretch	1615 cm^{-1}
medium, intense	Aromatic C=C	1515 cm^{-1}
medium	$-C-CH_3$ Stretch	1450 cm^{-1}
strong	-C-O Stretch	1305 cm^{-1}
strong, broad	phenolic -OH bending	1250 - 1200 cm^{-1}
weak	-OH Bending	1035 cm^{-1}
medium, intense	trisubstitution	1250 - 1200 cm^{-1}

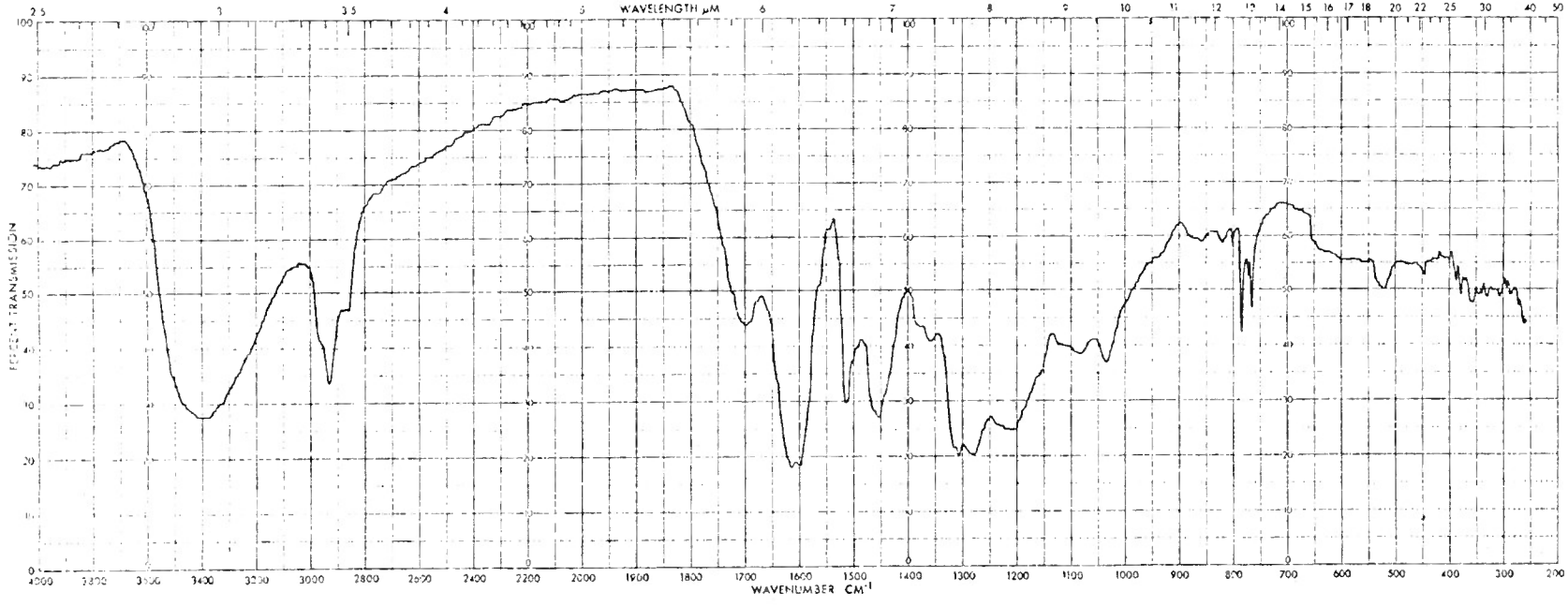


Fig. 16. IR Spectrum of Resole Polymer.

The first thermogram corresponding to the first extract was typical of a resin in its early stages of polymerization.

This uncured resin can further polymerize under the influence of heat and a large endotherm develops upon heating up to 115°C which is probably due to a large uptake of heat as the sample, in paste form, melted and evaporated volatile products. The exotherms at 148°C and 158°C corresponded to further polymerization. As the sample is heated curing is actually carried out in the cell. The polymer melts as molecules of water are volatilized and the resin increases in viscosity (Fig. 17). The effects of polymerization are clearly pointed out in the second and third thermograms (Figs. 18 and 19). In the second thermogram (second extraction) polymerization has proceeded to a more advanced stage and the hardening process starts at the first exothermic peak (83°C) in the resoles instead of at the higher temperatures noted for novalac resins at about 150°C.[33] The exothermic process corresponding to bridge formation occurred at 119°C and the endotherm starting at 130-165°C is possibly due to the evaporation of free phenol. (The thermogram (third extraction) made it possible to determine a glass transition temperature since this product was a solid material which could be properly packed in the heating pan.) There was no exothermic peaks present in the third thermogram characteristic of polymerization of resins. The sample geometry and also the heating rate has a significant effect on establishing a base line and glass transition temperatures. The thermogram thus indicated that the polymer was formed and cured but not in the three-dimensional state that would be insoluble and infusible. The polymer formed as indicated was possibly the b-stage

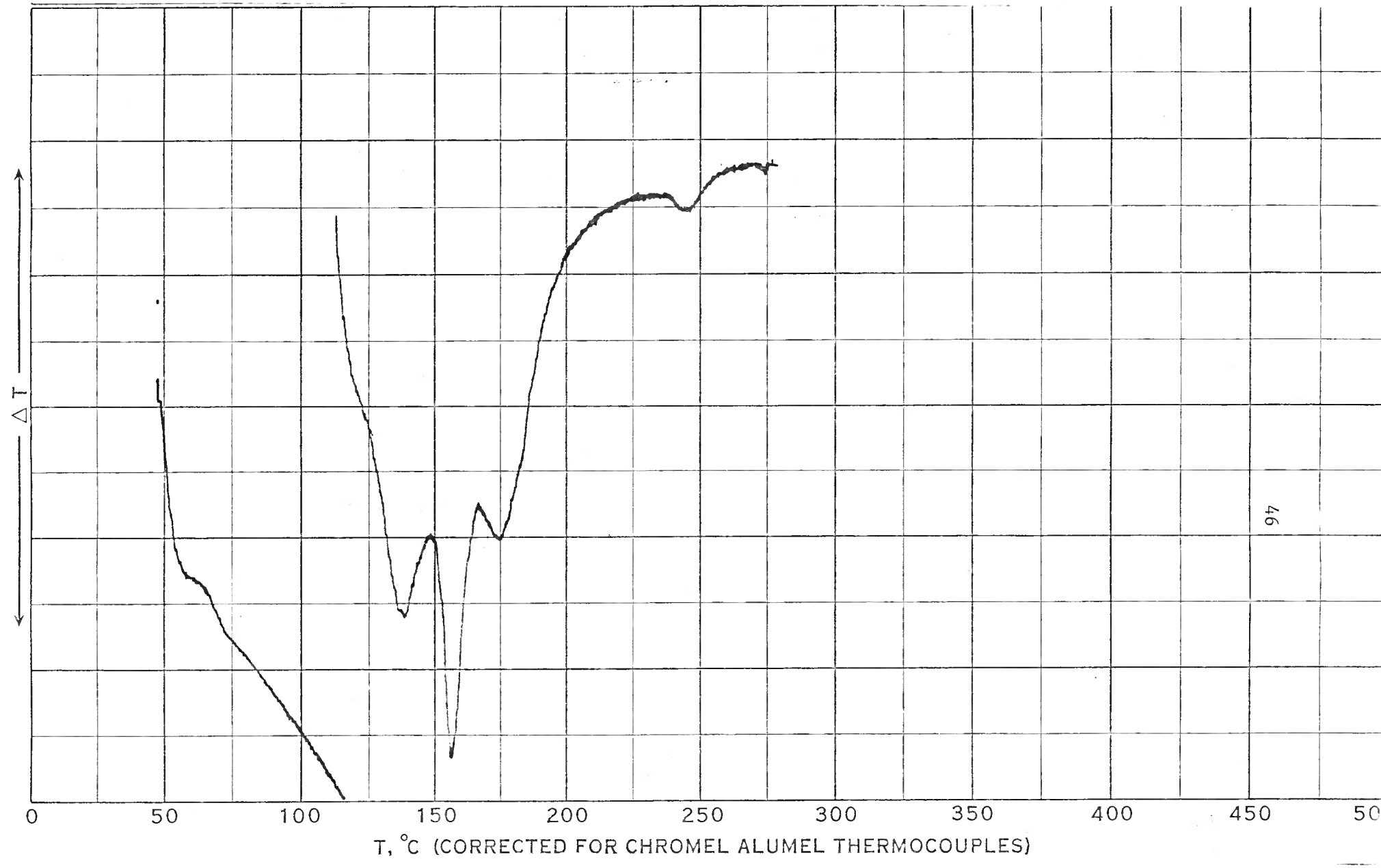


Fig. 17. Thermogram of First Extract from Resin Kettle.

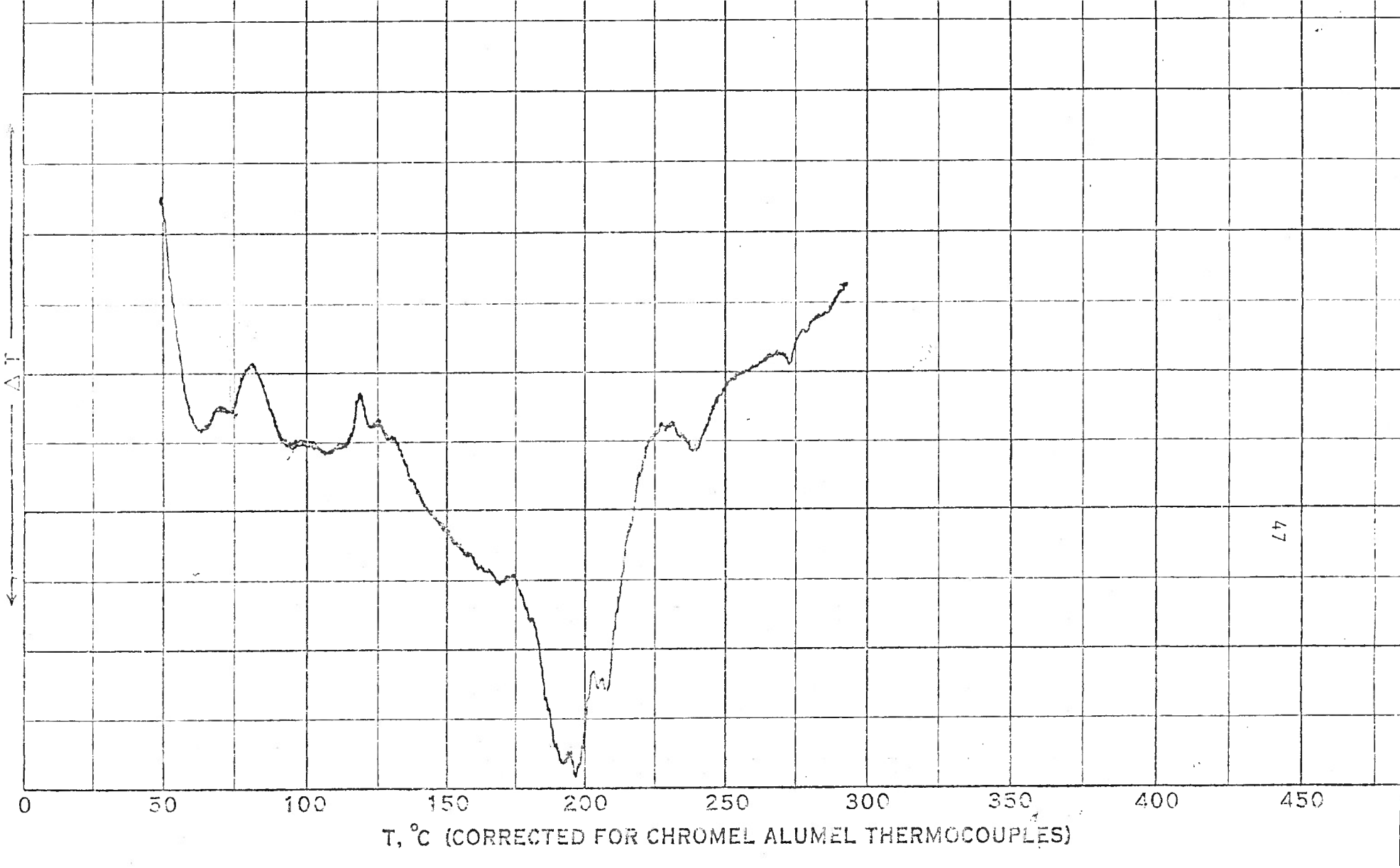


Fig. 18. Thermogram of Second Extract from Resin Kettle.

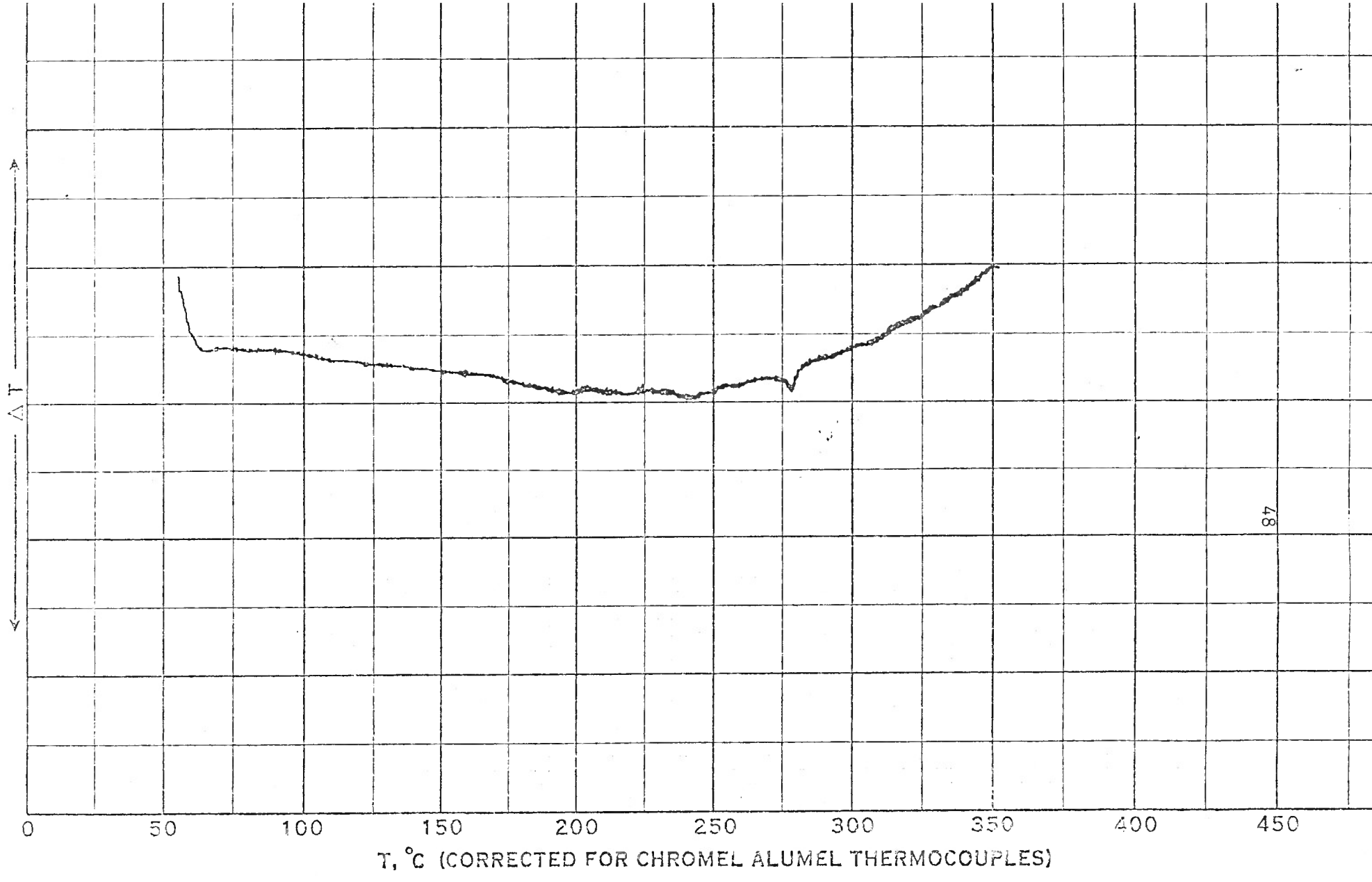


Fig. 19. Thermogram of Third Extract.

resitol which could be heated to the thermosetting resin. The usefulness of this polymer would depend on its molecular weight.

The Rast method was used for determining the molecular weights of the resitol, and it depends on the molar lowering in the melting point of a solvent (usually camphor) with formation of a solid solution. A polymer sample was weighed and placed in the test tube. The melting point of camphor used was determined to be 170°C. The camphor served as the solvent and both the camphor and polymer were heated to obtain a homogeneous mixture. Camphor is a waxy-like solid which had to be scraped from the test tube and placed on a clean watch glass and powdered. This process was necessary to crush the material to a state which allowed it to be placed in a capillary tube. Once the tube was filled with the sample about 1 mm high, its melting point was determined. The difference in the two melting points gives the exact depression in the melting point of the pure solvent (camphor) caused by the dissolved polymeric material.

The following equation was used to determine the number-average molecular weight ($\overline{Mn}$).

$$\overline{Mn} = \frac{K_m \times w \times 1000}{\Delta \times W} \qquad (3)$$

Three runs were made to get a close approximation of the molecular weight from this method. The runs yielded molecular weights of 900, 993, and 796. The average of these runs gave a number-average molecular weight of 896.

Galbraith Laboratories reported an analytical analysis of 70.42% C and 6.56% H and a molecular weight of 935 by vapor phase Osmometry.

K_m = molar depression constant W = weight of camphor

w = weight of polymer Δ = depression of melting point

EXPERIMENTAL

Extraction of Phenols from Pyrolytic Oils.--Procedure (A). Project B-469 condenser oil (84g) was extracted with 100 ml of deionized water. Two layers were formed after vigorous agitation. After allowing the two layers to completely separate, the aqueous layer was drawn off and discarded. The insoluble layer was then further extracted with 25 ml of 1.5 N $NaHCO_3$, and the resulting two layers that formed were again separated. After discarding the aqueous layer, 25 ml of 2.5 N NaOH was used to extract the remaining insoluble material. This material was completely soluble in NaOH. Next, the soluble solution of NaOH and pyrolytic oil was treated with 5% HCl until the basic solution was completely neutralized. There was noted a color change from dark brown to a very light rust brown color. Two layers were formed and the insoluble layer was separated. The neutralized solution was extracted with 20 ml portions of diethyl ether. Each of the fractions were placed in a ground glass round-bottomed flask and rotary evaporated to obtain 4.01 g of extracted phenols. A portion of the phenol sample was prepared for Capillary Gas Chromatography analysis: extracted phenols (0.5 to 1 ml) were dissolved in acetone and a 0.5 µl sample was injected in the capillary gas chromatograph.

Procedure (B). Pyrolytic oil (84g) was extracted with 100 ml of deionized water in two successive 50 ml extractions. Two layers were formed: the aqueous layer was discarded and the insoluble layer was then treated with 10 ml of 5% NaOH in 2 repeated extractions. The insoluble layer was then extracted with ether and no phase separation was noted.

This result was reproducible.

Procedure (C). Pyrolytic oil (84g) was extracted with 100 ml of deionized water in two successive 50 ml extractions after which two layers were formed and the aqueous layer removed. To the insoluble layer, 25 ml of 5% NaOH solution was added. Two layers were again formed and the soluble layer was removed. The NaOH insoluble layer was then treated with 25 ml of 5% $NaHCO_3$ solution. The soluble layer was again removed and the insoluble layer extracted with 20 ml of diethyl ether in 2 successive extractions. The aqueous layer was discarded and the organic layer was prepared for infrared analysis.

Preparation for Infrared Analysis.--The organic layer was rotary evaporated to obtain 2.34 g of a dark brown liquid. A portion of the recovered sample (1-2 ml) was placed in a small test tube, dissolved in methylene chloride and evaporated down in a water bath. The solution was then redissolved with methylene chloride and dried over a small amount of $MgSO_4$ for 24 hrs. The mixture was then filtered to remove particles of the drying agent.

Procedure (D). Pyrolytic oil (84g) was extracted with 25 ml of 5% NaOH. Two layers were formed and the insoluble layer discarded. HCl solution (5%, 20 ml) was then added to the soluble fraction. There was a slight color change from a dark brown to lighter brown. Next, 25 ml of 5% $NaHCO_3$ was added and two layers were formed. The $NaHCO_3$ insoluble layer was evaporated and there were 7.5 grams of a dark brown liquid material recovered. The $NaHCO_3$ soluble layer was discarded, and the sample material was prepared for infrared analysis.

Preparation for Infrared Analysis.--2 ml of the recovered material

was dissolved in CCl_4 and evaporated down in a water bath and redissolved in CCl_4. This solution was dried over $MgSO_4$ for 24 hrs and filtered.

Procedure (E). Pyrolytic oil (84g) was first extracted with 50 ml of deionized water. Two layers were immediately formed. The soluble layer was discarded and the insoluble layer was then treated with a fresh sample of 5% NaOH (25 ml). The insoluble fraction was completely soluble and two layers were not formed. Twenty-five (25) ml of $NaHCO_3$ (5%) was used in the next step of the separation, and phase distinction was not possible again. Finally, 20 ml of diethyl ether used in 10 ml portions was added to the separatory funnel and agitated. An oily-like, dark brown sample (2.42g) was recovered after rotary evaporation of ether. This sample was prepared for infrared analysis in accordance with procedure (A).

Procedure (F). Forty (40) gram samples of pyrolytic oils were extracted with 100 ml of the water heated to 45°C, 60°C, and 80°C. Each water extract was then further extracted with ether and rotary evaporated. Samples of .68, 1.0 and 1.2 grams were collected, consecutively. Next, GC/MS was run on a sample from the 60°C extraction and infrared analysis run on each of the extracts (Fig. 7, Table 7).

Procedure (G). Deionized water (500 ml) was heated to a temperature of 45°C and 50 ml used to extract 84 grams of pyrolytic oil. The insoluble fraction was then treated with 25 ml of a 5% solution of NaOH. The separatory funnel was agitated and allowed to stand to effect proper separation. Two phases were noted and the soluble layer removed. The insoluble fraction was extracted with 40 ml of ether and distinction between phases was not possible. After allowing time for the ether layer

to separate, there was a very dark semi-solid formed. The ether layer was drawn off, evaporated, and 4.62 grams of a dark black solid was obtained after allowing the sample to air dry for 48 hrs.

The soluble NaOH layer was then treated with 25 ml of 5% $NaHCO_3$ solution. Dark particles formed in the mixture which were filtered with a Buchner funnel. The recovered sample was an oily-like solid (4.0 grams), which could not be dried to a grindable solid. A portion of this material was then prepared for infrared analysis by procedure (A).

Extraction of Pyrolytic Oil Sample Using Continuous Liquid-Liquid Extraction.--This process was used in conjunction with procedure (A). After the NaOH-pyrolytic oil fraction was neutralized, a portion of the soluble aqueous layer, about 2-300 ml was placed in the bottom half of the continuous liquid-liquid extractor. The sample was extracted for 4 hrs, and after evaporation of the ether there was obtained 1.65 grams of phenolic extract.

Polymerization of a Cresol-Formaldehyde Resole Resin Using Shelf Reagents.--m-Cresol (50 grams, 1.37 moles), 130 grams (7.6 moles) of 37% formaldehyde solution (formalin), and 7.5 grams of 25% ammonia (specific gravity .90) were charged to a 500 ml resin kettle. The kettle was equipped with a mechanical stirrer, thermometer, dropping separatory funnel and glass stoppers. The mixture was refluxed for 1½ - 2 hrs with stirring. Next, water was removed from the mixture under reduced pressure and distillation (vacuum distillation) by raising the temperature of the reaction from 45°C to 75-78°C. The reaction mixture was then heated until it was stiff enough to slow the mechanical stirrer. There was 196 grams of resinous material recovered which was dried for 4 hrs.

Polymerization of a Resole Resin from Extracted Phenols.--To a 500 ml resin kettle equipped with thermometer, mechanical stirrer and glass stoppers, 35 grams (0.4 moles) of extracted phenols, 42 grams (1.4 moles) of 37% formalin, 4 grams of water, and 2 grams of barium hydroxide octahydrate were added. This mixture was stirred and maintained at 70°C for 2 hrs. Next, a sufficient amount of oxalic acid was added to bring the pH to 6-7. The water was removed by distillation under reduced pressure. At a temperature no higher than 70°C, 1-2 ml samples were withdrawn every 15 minutes to check the extent of condensation. The end product was taken when the resin became brittle and non-tacky upon cooling. A brown resinous material (7.9 g) was obtained from the resin kettle, and a small amount of a white solid collected in the distillation flask (ca. 0.5 g).

Characterization of Polymeric Materials.--Solubility.--Small amounts of the resinous material collected from the resin kettle were placed in small beakers. Each sample was then tested for solubility in formic acid, benzene, ethyl and methyl alcohol, phenol, and acetone. Acetone and phenol were the only solvents which appreciably dissolved the material and a small amount of white insoluble material remained.

Next, the entire 7.9 grams of resinous material was partially dissolved in acetone, and the mixture filtered through a fritted glass funnel to obtain 1.34 grams of a white solid material. The acetone solution was rotary evaporated to obtain 6.0 grams of a brown solid, which was dried for 4 hrs. IR results are reported in Tables 10 and 11.

DSC.-- Differential Scanning Calorimetry. Each of the three extracts taken during polymerization were also analyzed by differential scanning

calorimetry, and an infrared spectrum were taken of the final resinous product (Table 11).

Gel Time.--A finely ground sample of each of the recovered materials were placed on a hot plate which was at a temperature of 150°C. A spatula was used to work the resin slowly back and forth on the hot plate. The time taken for the brown polymeric sample to gel was 35 sec. The white material did not gel.

Molecular Weight Determination by Rast Method.--The weight of a small, clean, dry test tube (8 by 50 mm) was determined to be 6.044 grams. Approximately 50 mg of the sample material was weighed out to be .047 grams, and placed in the tube to give a combined weight of 6.091 grams. Next, about 0.5 grams of camphor (mp 17°C) was weighed out at .495 grams and added to the contents of the tube. The total weight of test tube, polymer sample, and camphor was 6.583 grams. The contents of the tube were melted over a low flame to a clear liquid. (Caution was taken not to heat the mixture too long.) After cooling to a homogeneous waxy solid, the contents of the tube were removed to a clean watch glass. The material was then powdered and its melting point determined by the capillary tube method. The capillary tube in which the melting point is determined should contain a column of the material only 1 mm high, and the column must be tightly packed by means of a smaller capillary tube. The temperature at which the solution became entirely clear of solid was taken as the melting point. The melting point of the original camphor was determined by the capillary tube method also. The difference in these two melting points gave the depression in melting point of the camphor used by the polymer.

CONCLUSION

The white material produced did not have any of the inherent qualities of resole polymers. This material was relatively unreactive to solubility studies and was not extensively investigated. This material could be a fairly crosslinked co-polymer from a number of components present in the oils. If polymerization is allowed to occur with phenol and formaldehyde, there should be a formation of crosslinked polymer composed of phenol-formaldehyde units. However, if a mixture of phenols with varying degrees of reaction toward polymerization are reacted together, there should then be a compound formed which has incorporated the molecules of the different phenols into a straight or branched chain. This would depend on the reactivity and structure of the compounds present.

Furthermore, the production of a homogeneous polymer would be a likely result from this polymerization. Instead a heterogeneous system was obtained. Again, this could have formed from the various components which had similar reactivities toward formaldehyde. As the reaction proceeded, each compound could have come together to form a co-polymer with similar properties. When these compounds have been depleted there could be some phenolic compounds present which have a lower reactivity to polymerization that could possibly react with any remaining formaldehyde. There could in theory exist a hard and soft co-polymer from the mixture with each having different characteristics. Therefore, if further studies are undertaken, there should be an investigation of this

possibility or the range of the types of phenols extracted could be more selective.

The separation of phenolic components from pyrolytic oil was performed by means of a solubility scheme using solvent extraction techniques. This method did show good capability for the separation of the components; however, other methods of separation should be investigated to further optimize the process of separation. Parameters which affect the amount of phenol extracted should be determined; temperature and pH considered, and some chromatographic techniques should be used.

Polymerization of the phenolic components from pyrolytic oil gave a resin with a molecular weight in the range necessary for resole type polymers. The product was easily obtained from the reaction kettle and characterization achieved.

REFERENCES

1. Keutgen, W. A., "Phenolic Resins," Encyclopedia of Polymeric Science and Technology, John Wiley and Sons, Inc., 1966, Vol. X, p. 1.

2. Ibid., p. 2.

3. Ibid., p. 3.

4. A. Michael, J. Amer. Chem. Soc., 5, 338 (1883-1884).

5. Keutgen, W. A., "Phenolic Resins," Encyclopedia of Polymeric Science and Technology, John Wiley and Sons, Inc., 1966, Vol. X, p. 2.

6. A. Luft, Ger Pat. 140 552 (1902); U.S. Pat 735278 (1903).

7. Keutgen, W. A., "Phenolic Resins," Encyclopedia of Polymeric Science and Technology, John Wiley and Sons, Inc., 1966, Vol. X, p. 2.

8. L. H. Backeland, J. Ind. Eng. Chem., 1, 3, 750 (1909).

9. Keutgen, W. A., "Phenolic Resins," Encyclopedia of Polymeric Science and Technology, John Wiley and Sons, Inc., 1966, Vol. X, p. 9.

10. Hawley, L. F. and Wise, L. E., "The Chemistry of Wood," Chemical Catalog Co. (1926), p. 64.

11. L. V. Panasyuk, L. V. Travleeva, V. G. Panasyuk, Khim. Drev. 1, 301-4 (1968); Chem. Abst. 71, 14345.

12. K. I. Shmulevskaya and A. A. Liverovskii. Tr. Leningr. Lesotekhn. Akad., 1963 (102), 211-20; Wood Products, 51, 7749.

13. A. K. Slavyanskii and V. N. Piyalkin, Izv. Vysshikk Uchebn. Zanedenii, Lesn. Zh. 5, No. 2, 124-6 (1962); Wood Products, 49, 7497.

14. M. B. Polk, Personal Communication, 1978.

15. N. A. Skoog and D. M. West, "Principles of Instrumental Analysis," Holt, Rienhart and Winston, Inc. New York, N. Y., 1971, p. 654.

16. Hiram McCann, J. Fradas, R. G. Van Berkik, Modern Plastic, 40 (5), 102 (1963).

17. Keutgen, W. A., "Phenolic Resins," Encyclopedia of Polymer Science and Technology, John Wiley and Sons, Inc., 1966, Vol. X, p. 6.

18. D. Braun, H. Cherdron, W. Kern, "Technique of Polymer Synthesis and Characterization," Wiley-Interscience, New York-London-Sidney-Toronto, 1972, p. 61.

19. Odin, G. G., "Principles of Polymerization," New York, McGraw-Hill, 1970, Vol. XXIII, p. 114.

20. Ibid., p. 115.

21. Keutgen, W. A., "Phenolic Resins," Encyclopedia of Polymer Science and Technology, John Wiley and Sons, Inc., 1966, Vol. X, p. 26.

22. H. S. Lilley, J. Soc. Chem. Ind., 67, 196 (1948).

23. M. B. Polk, Atlanta University Chemistry Department, Quarterly Report, Grant No. R-804 440 010, Atlanta, GA., June 1977.

24. R. T. Morrison and R. N. Boyd, "Organic Chemistry," 3rd Ed., Allyn and Bacon, Inc., Boston, N. Y., 1973, p. 788.

25. M. B. Polk, Personal Communication, 1978.

26. Keutgen, W. A., "Phenolic Resons," Encyclopedia of Polymer Science and Technology, John Wiley and Sons, Inc., 1966, Vol. X, p. 3.

27. Kauman, H. S. and J. J. Falcetta, "Introduction to Polymer Science and Technology; An SPE Textbook," John Wiley and Sons, New York, 1977, p. 27.

28. Sandler, S. and Wolf, K., "Polymer Synthesis," 2, Academic Press, New York, N. Y., (1977), 223.

29. H. H. Willard, L. L. Merrit, J. A. Dean, "Instrumental Methods of Analysis," 5th Ed., D. Van Nostrand Co., New York, N. Y., 1974.

30. R. E. Kagarise, L. A. Weinberger, "Infrared Spectra of Plastic and Resins," U. S. Dept. of Comm., OTS Bulletin, No. PB1114381, Washington, D. C., 1954.

31. L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, New York, N. Y., 1958.

32. Z. Katovic, J. Applied Polymer Science, II, pp. 85-93, (1967).

33. V. A. Popov, I. S. Druyan, B. C. Varshal, Sonut Plastic, 1964, No. 5, 21.